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LASER-INDUCED-FLUORESCENCE INSPECTION OF POLYURETHANE AND RELATED MATERIALS

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FINAL REPORT/PHASE 1
28 March 1986 - 15 November 1988
SwRI Project 17-7958-828

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PREPARED FOR
U.S. Army Belvoir Research, Development
and Engineering Center
STRBE-VU
Ft. Belvoir, Virginia 22060-5606

ATTENTION
Messrs. Henry Feuer and Paul Touchet

PREPARED BY
R.H. Hill Jr.
Group Leader
Laser Applications

PERFORMED AS A SPECIAL TASK FOR THE NONDESTRUCTIVE TESTING INFORMATION ANALYSIS CENTER
UNDER CONTRACT NO. DLA 900-84-C-0910 CLIN 0001AX, MODS: P00043, P00046, AND P00060

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EXECUTIVE SUMMARY

Laser-induced fluorescence has been used as the basis for a new nondestructive-inspection technique. A strong correlation between laser-induced-fluorescence intensity and tensile strength of several polyurethane-based systems has been demonstrated. Various parameters, such as excitation and detection wavelengths, have been experimentally investigated. Successful laboratory experiments employing fiber-optic bundles indicate that practical implementation of this method is possible. A portable instrument to determine the physical condition of fabric-reinforced polyurethane fuel tanks used by the U.S. Army is one immediate application, but the method may also be applicable for use on other elastomeric materials.



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TRADE NAMES

Use of trade names or manufacturers in this report does not constitute an official endorsement or approval of the use of such hardware or software.

PREFACE

The concept of laser-induced-fluorescence inspection as applied to materials of interest to the U.S. Army was originally outlined in Southwest Research Institute (SwRI) Unsolicited Proposal 15-3363, 11 Oct 85, "Laser-Induced-Fluorescence Inspection of Urethane and Related Materials," which was funded (SwRI Project Number 17-7958-828; through the Nondestructive Testing Information Analysis Center (NTIAC) as a special task of the NTIAC contract No. DLA 900-84-C-0910, CLIN 0001AX (Reference Modifications P00043, P00046, P00060) by MIPR #IA-12-0004. Technical contacts were Messrs. Henry Feuer and Paul Touchet of the Rubber and Coated Fabrics Research Group, Materials, Fuels, and Lubricants Laboratory, U.S. Army Belvoir Research, Development, and Engineering Center, (STRBE-VU), Ft. Belvoir, VA 22060-5606. Most of the degraded (artificially aged) samples, as well as the relevant tensile-strength and elongation data, were supplied by the sponsor.

A developmental-prototype phase was originally mentioned as Phase B of SwRI Proposal 15-3363. The cost proposal for the developmental prototype was submitted to the Belvoir Research, Development, and Engineering Center under SwRI Proposal 15-3363B, 30 Sept 87.

A patent application [No. 917,959] has been filed by SwRI covering this basic method for inspection of polymer-based materials. SwRI has been notified by the patent office that the application has been allowed.

TABLE OF CONTENTS

	Page
LIST OF FIGURES	viii
LIST OF TABLES	xi
I. INTRODUCTION	1
A. The Problem	1
B. Background	1
1. Polymer Degradation	1
2. Laser-Induced Luminescence	2
3. Literature Survey	3
C. Research Approach	4
II. BASIC RESEARCH	5
A. Introduction	5
B. Samples	5
C. Equipment and Procedures	5
1. Laser-Induced Fluorescence	5
2. Reflectance	6
D. Data	6
1. Laser-Induced Fluorescence	6
2. Reflectance	8
E. Results	8
1. Laser-Induced Fluorescence	8
2. Reflectance	8
3. Discussion	9
III. INTEGRATED FLUORESCENCE AND OPTIMIZATION STUDIES	10
A. Introduction	10
B. Samples	10
C. Equipment and Procedures	10
D. Data	11
1. Integrated Fluorescence	11
2. Polarization	11
3. Filter Optimization	11
4. Lock-in Mode versus AC-Voltmeter Mode	11
5. Backing Material	12
6. Reflectance/Integrated-Fluorescence Ratio	12
E. Results	12

TABLE OF CONTENTS (Cont'd.)

	<u>Page</u>
IV. BIFURCATED FIBER-OPTIC BUNDLE EXPERIMENTS	13
A. Introduction	13
B. Samples	13
C. Equipment and Procedures	13
D. Data	13
1. Stand-off Distance	13
2. Interference Filters	14
3. Filter Optimization	14
4. Concept Demonstration	14
5. Linearity	14
6. Correlation of Laser-Induced Fluorescence with Tensile Strength	15
E. Results	15
V. CONCLUSIONS AND RECOMMENDATIONS	16
VI. REFERENCES	18
A. Footnotes	18
B. Bibliography	19
VII. TABLES AND FIGURES	21
APPENDIX	

LIST OF FIGURES

(Note: All tables and figures are grouped together in Section VII.)

Figure		Page
1	EXPERIMENTAL APPARATUS FOR BASIC RESEARCH UTILIZING LASER-INDUCED FLUORESCENCE	26
2A	LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE (Ex: 488 nm; Det: 577 nm; Samples: UA, UB, UC, G; Aging Method: Hot Water)	27
2B	LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE (Ex: 488 nm, Det: 577 nm, Samples: G; Aging Method: Hot Water; Comments: Expanded scale of Figure 2A)	28
2C	LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE (Ex: 488 nm; Det: 577 nm; Samples: PU1, PU2, PU1S, PU2S; Aging Method: Hot Water)	29
2D	LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE (Ex: 488 nm; Det: 577 nm; Samples: PU1, PU2; Aging Method: Hot water; Comments: Expanded scale of Figure 2C)	30
2E	LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE (Ex: 488 nm; Det: 577 nm; Samples: EST; Aging Method: Hot water)	31
2F	LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE (Ex: 488 nm; Det: 577 nm; Samples: LU1, LU2; Aging Method: Hot water; Comments: Note that age coordinate slightly differs from other graphs)	32
3A	LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE (Ex: 488 nm; Det: 577 nm; Samples: UA, UB, UC, G, GF; Aging Method: Weatherometer)	33
3B	LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE (Ex: 488 nm; Det: 577 nm; Samples: PU1, PU2, PU1S, PU2S; Aging Method: Weatherometer)	34
3C	LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE (Ex: 488 nm; Det: 577 nm; Samples: PU1, PU2; Aging Method: Weatherometer; Comments: Expanded scale of Figure 3B)	35
4A	LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE (Ex: 351+363 nm; Det: 580 nm; Samples: PU1S, PU2S; Aging Method: Hot Water)	36
4B	LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE (Ex: 351+363 nm; Det: 580 nm; Samples: PU1, PU2; Aging Method: Hot Water)	37

LIST OF FIGURES (Cont'd.)

(Note: All tables and figures are grouped together in Section VII.)

Figure		Page
5	RELATIVE LASER-INDUCED-FLUORESCENCE RATIO AS A FUNCTION OF EXCITATION WAVELENGTH (Samples: UB (400 hrs), UB (unaged); Aging Method: Weatherometer)	38
6A	LASER-INDUCED FLUORESCENCE AS A FUNCTION OF LASER IRRADIATION TIME (Ex: 488 nm; Det: 577 nm; Sample: UA (21 days); Aging Method: Hot Water)	39
6B	LASER-INDUCED FLUORESCENCE AS A FUNCTION OF LASER IRRADIATION TIME (Ex: 488 nm; Det: 577 nm; Sample: UB (400 hrs); Aging Method: Weatherometer; Comments: Laser power density was less than for Figure 6A)	40
7A	REFLECTANCE AS A FUNCTION OF WAVELENGTH (Samples: UB (unaged) and UB (70 days); Aging Method: Hot Water; Comments: Anomalies at approximately 360 nm and 860 nm are instrumental artifacts)	41
7B	REFLECTANCE AT 633 NM AS A FUNCTION OF AGE (Ex: 633 nm; Det: 633 nm; Samples: UB; Aging Method: Hot Water)	42
7C	"X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: UA, UB, UC, G; Aging Method: Hot Water)	43
7D	"X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: PU1, PU1S, PU2, PU2S; Aging Method: Hot Water)	44
7E	"X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: EST; Aging Method: Hot Water)	45
7F	"X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: LU2; Aging Method: Hot Water; Comments: Note that age coordinate slightly differs from other graphs)	46
7G	"X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: UA, UB, UC, G; Aging Method: Weatherometer)	47
7H	"X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: PU1, PU1S, PU2, PU2S; Aging Method: Weatherometer)	48
7I	"X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: GF; Aging Method: Weatherometer)	49
8A	TENSILE STRENGTH AS A FUNCTION OF AGE (Samples: UA, UB, UC, G; Aging Method: Hot Water; Comments: Data courtesy of U.S. Army Belvoir R,D,&E Center)	50

LIST OF FIGURES (Cont'd.)

(Note: All tables and figures are grouped together in Section VII.)

Figure		Page
8B	TENSILE STRENGTH AS A FUNCTION OF AGE (Samples: PU1, PU2, PU1S, PU2S; Aging Method: Hot Water; Comments: Data courtesy of U.S. Army Belvoir R,D,&E Center)	51
9A	ELONGATION AS A FUNCTION OF AGE (Samples: UA, UB, UC, G; Aging Method: Hot Water; Comments: Data courtesy of U.S. Army Belvoir R,D,&E Center)	52
9B	ELONGATION AS A FUNCTION OF AGE (Samples: PU1, PU2, PU1S, PU2S; Aging Method: Hot Water; Comments: Data courtesy of U.S. Army Belvoir R,D,&E Center)	53
10	EXPERIMENTAL APPARATUS FOR MEASURING INTEGRATED FLUORESCENCE	54
11A	INTEGRATED DIFFERENTIABILITY (Ex: 543.5 nm; Samples: UB; Aging Method: Weatherometer)	55
11B	INTEGRATED DIFFERENTIABILITY (Ex: 488 nm; Samples: UB; Aging Method: Weatherometer)	56
12	EXPERIMENTAL APPARATUS USING A BIFURCATED FIBER-OPTIC BUNDLE	57
13A	INTEGRATED LASER-INDUCED-FLUORESCENCE INTENSITY MEASURED THROUGH A FIBER-OPTIC BUNDLE AS A FUNCTION OF AGE (Ex: 488 nm; Det: >577 nm; Samples: UA, UB, UC, G; Aging Method: Hot Water)	58
13B	INTEGRATED LASER-INDUCED-FLUORESCENCE INTENSITY MEASURED THROUGH A FIBER-OPTIC BUNDLE AS A FUNCTION OF AGE (Ex: 488 nm; Det: >577 nm; Samples: G; Aging Method: Hot Water; Comments: Expanded scale of Figure 13A)	59
14	LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF LASER POWER (Ex: 488 nm; Det: >577 nm; Samples: UB (unaged), UB (21 days), UB (70 days); Aging Method: Hot Water; Comments: Logarithmic presentation)	60
15A	SCATTER DIAGRAM OF LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF TENSILE STRENGTH (Ex: 488 nm; Det: 570 nm; Samples: UA; Aging Method: Hot Water; Comments: Straight line is the linear least-squares fit neglecting data point from the unaged sample)	61
15B	SCATTER DIAGRAM OF LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF TENSILE STRENGTH (Ex: 488 nm; Det: 570 nm; Samples: UB; Aging Method: Hot Water; Comments: Straight line is the linear least-squares fit neglecting data point from the unaged sample)	62

LIST OF FIGURES (Cont'd.)

(Note: All tables and figures are grouped together in Section VII.)

Figure		Page
15C	SCATTER DIAGRAM OF LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF TENSILE STRENGTH (Ex: 488 nm; Det: 570 nm; Samples: UC; Aging Method: Hot Water; Comments: Straight line is the linear least-squares fit neglecting data point from the unaged sample)	63
15D	SCATTER DIAGRAM OF LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF TENSILE STRENGTH (Ex: 488 nm; Det: 570 nm; Samples: G; Aging Method: Hot Water; Comments: Straight line is for ease of viewing, see text for discussion)	64
15E	SCATTER DIAGRAM OF LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF TENSILE STRENGTH (Ex: 488 nm; Det: 570 nm; Samples: UA, UB, UC, G; Aging Method: Hot Water; Comments: Data displayed are those of the previous scatter diagrams, with the data points simply connected for ease of viewing)	65
16	CONCEPTUAL DIAGRAM OF PROPOSED DEVELOPMENTAL PROTOTYPE	66

LIST OF TABLES

(Note: All tables and figures are grouped together in Section VII.)

Table		Page
I	SAMPLES	22
II	FLUOROPHORE PHOTOINITIATION IN POLYURETHANE	23
III	DIFFERENTIATION OPTIMIZATION WAVELENGTHS	24
IV	COMPARISON OF THE LASER-INDUCED FLUORESCENCE AND REFLECTANCE METHODS FOR DETERMINATION OF AGING	25
A1	COLORS OF UNAGED SAMPLES	A1

I. INTRODUCTION

A. The Problem

The U.S. Army currently has a large number of fabric-reinforced elastomer tanks, ranging in size from 100 gallons to 200,000 gallons, used for storing fuel or other liquids. These tanks must hold liquids for extended periods of time while exposed to the elements and then be folded and stored worldwide in crates for years before being needed again. The combination of heat and humidity is very deleterious to the materials used in the construction of these tanks. Although the tanks are drained after use and prior to storage, residual liquid usually remains in them. Exposure to the liquid can degrade the polymer after a long period of time and cause leakage. The current procedure is to discard tanks which have been stored for five years or more, even if they have never been in service. Nondestructive-inspection techniques for determining the condition of these tanks are needed. Additionally, other elastomer-coated fabric items, such as pneumatic boats, pontoons, decoys, shelters, or raincoats, may be tested by similar.

In previous work (Contract No. DAAK70-85-C-0007) at Southwest Research Institute (SWRI), a portable surface-resistivity meter was developed to evaluate physical condition of fabric-reinforced polyurethane fuel tanks. The present project, is based on a completely different concept, laser-induced fluorescence, addresses the same problem; additionally, this technique may be applied to many other problems.

B. Background

1. Polymer Degradation

Polyurethanes are a broad class of chemically divergent polymers. The two main subgroups are ether-based polyurethanes comprising flexible polyether segments joined by rigid urethane segments and ester-based polyurethanes where flexible aliphatic or aromatic polyester segments are joined by urethane links. The types and lengths of flexible and rigid segments in polyurethane determine whether the resins are soft, rubbery, or glassy. Polyurethanes are widely employed as films, foams, moldings, and specialty items. In general, there are several mechanisms that initiate degradation in polyurethanes [Ref. 1]. Hydrolysis: In ether-based polyurethanes, only the urethane linkage undergoes hydrolysis, and quite severe conditions are required. In contrast, ester-based polyurethanes may undergo scission at either ester or urethane linkages; in fact, the ester group is an order of magnitude more sensitive to hydrolysis than the urethane linkage. Chain cleavage is accompanied by an increase in crystallinity which accentuates changes in mechanical properties. Thermal reactions: At temperatures above 150°C, the urethane link cleaves to give a variety of reaction products. In the presence of oxygen, all polyurethanes oxidize, especially in the flexible segments. Ether segments are particularly prone to oxidation. Photoreactions: In general, all polyurethanes are light-sensitive to some degree, from either direct photoreactions or complex reactions involving free radicals. The wavelengths and power densities of the light involved are very important parameters in these processes.

Other elastomers may have better weathering characteristics than the ester-based or ether-based polyurethanes originally studied. Therefore, limited measurements on several other elastomers were also conducted during the course of the work.

2. Laser-Induced Luminescence

Laser-induced luminescence (LIL) is emission of light resulting from absorption of laser energy by a substance. The wavelengths of the reradiated light contain a major component at the wavelength of the exciting laser light (reflected light), but there are also many new wavelengths present (luminescence) that are determined by the molecular structure of the substance. Laser-induced luminescence includes both laser-induced fluorescence (LIF), which is fast luminescence occurring on time scales of the order of nanoseconds, and laser-induced phosphorescence (LIP), which is slower luminescence occurring on time scales as long as several seconds. The luminescence spectrum is not only a function of time, but also a function of the excitation spectrum. Fluorescence and phosphorescence have been studied for a number of years and have been used in numerous ways in the laboratory environment. Laser-induced luminescence is finding widespread use in many new and diverse applications; for example, it is currently being used to study energy redistribution collisions in vapors, for fingerprint detection, to map flowfields in chemical lasers, and in medical applications. In recent years, technological advances have increased reliability and portability of lasers and also generally reduced costs; this is readily demonstrated by the wide use of helium-neon lasers in bar-code scanners found in many supermarkets.

In many applications, fluorescence dominates phosphorescence. Fluorescence is characterized by many spectra depending on the excitation wavelength. A fluorescent molecule emits a fluorescence spectrum after it absorbs radiation within its excitation spectrum. The spectral distribution of the fluorescent radiation is a physical and absolute characteristic of a given substance for a given excitation wavelength and is useful for qualitative considerations. The emission intensity of fluorescence at a given wavelength is useful for quantitative analysis with a given instrument after standardization. Quantitative measurements show that there is sometimes a very strong correlation between laser-induced luminescence and some physical characteristic of the material. Many times this is due to the fact that fluorescence reveals relationships (e.g., conjugation) between molecular functional groups; this is in contrast to infrared absorption techniques, which are mainly used to reveal presence of individual molecular functional groups. Because alteration of these relationships between certain molecular functional groups occur during degradation, laser-induced luminescence can be used to monitor degradation processes.

Polymer photophysics has received much attention recently [Ref. 2]. Molecules containing absorbing groups, called chromophores, undergo electronic transitions which result in the characteristic absorption of the compound. Chromophores occur naturally or may be artificially introduced as a label (e.g., a fluorescent-dye molecule) attached to the polymer. Commonly occurring chromophores include: Ether (-O-), Ester (-COOR), and Nitrile (-CN) with peak absorptions at 185 nm, 205 nm, and 160 nm, respectively [Ref. 3]. If these chromophores lose excess energy through nonradiative transitions

(such as heating), they are considered chromophores only; however, if excess energy is re-emitted as luminescence, chromophores can also be considered as fluorophores.

With the monochromaticity and power density available with lasers, molecular transitions that are not normally thought of as fluorescent can be probed. For instance, chromophores that exhibit ultraviolet absorption can sometimes be induced to fluoresce with laser excitation in the visible region of the spectrum; this effect can be very important from the viewpoint of practical implementation of instruments based on these properties.

COMMENT ON TERMINOLOGY: When a spectrum is dominated by the fluorescent component, luminescence is commonly referred to as fluorescence. A distinction is usually made only when the phosphorescence dominates or is intentionally measured after fluorescence has decayed. (A common example of this slightly ambiguous terminology is "fluorescent" paint--phosphorescence is actually the process that causes the paint to glow in the dark.)

3. Literature Survey

The versatility and sensitivity of luminescence as a technique in polymer chemistry stem from multiple aspects of interactions of the electronically excited states with their immediate environment [Ref. 4]. Luminescence has been used to study some thin-film polyurethane systems [Ref. 5] where it was found that luminescence characteristics may be very different, although absorption spectra may be very similar. These differences were dependent on the manufacturing processes because of the impurity concentrations. Fluorescence has also been used to monitor polymerization (viscosity) in systems such as methyl methacrylate [Ref. 6]. Use of fluorescent probes (dyes) has been investigated for similar applications. Fluorescent probes have been used in polyurethane systems [Refs. 7-8] as well as several other polymer systems [Refs. 9-11]. Disadvantages of adding fluorescent probes are (1) the material may also change in color, (2) interaction between the probe molecule and the polymer may adversely affect the polymer, and (3) some of the probe molecules may leach out as the polymer degrades, thus complicating interpretation of the data.

A research group in Helsinki has recently reported a new instrument (PEXSCANNER) that can be used to estimate the relative degree of cross-linking in polyethylene (PE) plastic. Their results were good for peroxide-linked polyethylene and in most cases for radiation-linked polyethylene. Their instrument used a helium-cadmium laser operating at 442 nm to induce fluorescence in the visible region of the spectrum; it was reported to have many interesting features that may be listed as follows:

- "-The measurement can be done quickly and in a nondestructive way
- With certain precautions, on-line measurements can be done
- Only relatively little sample preparation is required
- The readout is obtained electronically
- The measurements can be repeated for the same sample at will
- Operates both with peroxide-linked samples and with radiation linked samples (with reservations)."

The disadvantages that were reported are as follows:

- "-Does not work with carbon-black-filled samples
- Has to be calibrated for each material quality
- May be sensitive to geometrical factors in samples (edge effect, thickness variations for thin samples)
- Thin films produce only weak signals (unless samples are stacked)
- Measurement window has to be shielded against stray light
- Crystallinity changes may influence results." [Ref. 12]

C. Research Approach

A systematic research plan was established with the ultimate goal of developing an instrument capable of determining in the field degradation of fabric-reinforced elastomer fuel tanks. Basic research was conducted to determine if laser-induced-fluorescence intensity could be correlated to degraded mechanical characteristics. Laboratory experiments were conducted using standard spectroscopic techniques as described in Section II. A wide variety of samples was studied during this subtask. The next step was to determine if complex, bulky, and expensive laboratory equipment could be replaced with simpler, smaller, and lower-cost equipment; this work is described in Section III. Similar experiments were then conducted with the incident laser beam and resulting fluorescent light being conducted through fiber-optic bundles as described in Section IV. A smaller sample set was used during the latter subtasks. The next step, a demonstration prototype, is justified based on the results of this work.

II. BASIC RESEARCH

A. Introduction

Standard laboratory methods were used to measure laser-induced fluorescence, as well as reflectance, from sample materials that were supplied by the Ft. Belvoir Research, Development and Engineering Center.

B. Samples

Samples were artificially aged at Ft. Belvoir (1) by immersion in hot distilled water (160°F for periods up to 70 days), and (2) in a weatherometer (160°F with ultraviolet exposure and intermittent water spray for periods up to 500 hours); selected samples were also aged at SwRI using ultraviolet exposure (in a Q-Panel Co. weathering tester model QFS-40UV without water for periods up to 120 hours), in addition to the treatment performed by Ft. Belvoir. Tensile-strength and elongation data on many of the artificially aged samples were measured by personnel at Ft. Belvoir. A list of samples and nomenclature is shown in Table I. The samples included ester-based polyurethanes (UA, UB), ether-based polyurethanes (UC), and nitriles (G, GF) all of which were commercially available. Additionally, several carbon-filled ester-based polyurethanes (PU1), carbon-filled ether-based polyurethanes (PU2), silica-filled ester-based polyurethanes (PU1S), and silica-filled ether-based polyurethanes (PU2S) were manufactured at Ft. Belvoir. Several other samples, as listed in Table I, were also tested on a limited basis. The samples were tested as received from Ft. Belvoir with no further surface preparation; the samples had been slightly cleaned at Ft. Belvoir using a mild detergent and a toothbrush.

Samples were originally supplied to SwRI in a blind study, i.e., data for basic research were obtained before ages of the samples were revealed; however, to establish the relationship between laser-induced fluorescence and degradation, the necessary information was subsequently made available.

C. Equipment and Procedures

1. Laser-Induced Fluorescence

Several lasers were used in the studies, including a Spectra-Physics model 2025 argon-ion laser (operating at the wavelengths 351.1 nm + 363.8 nm, 457.9 nm, 488.0 nm, 501.7 nm, or 514.5 nm), an Omnicrome model 356XL helium-cadmium laser (325 nm), a PMS model LHGR-0050 helium-neon laser (543.5 nm), and a Spectra-Physics model 120 helium-neon laser (632.8 nm). Standard spectroscopic techniques were used to obtain laser-induced-fluorescence data. Fluorescent light was collected with a lens and focussed into a Bausch and Lomb model 33-86-77 spectrometer with a full-width-at-half-maximum bandwidth of 8 nm. The spectrometer wavelength could be held fixed or scanned. Appropriate Schott glass filters were used to reject scattered laser light. Initial measurements were conducted with a Keithley model 610B electrometer to monitor the photocurrent from a RCA model 1P21 photomultiplier-tube detector as depicted in Figure 1; however, because of the inherent advantages associated with modulated measurements, the electronic detection method was upgraded as follows. A Princeton Applied Research (PAR)

model 125 light chopper modulated the laser light. Photocurrent from the photomultiplier tube was used to develop a voltage across a load resistor, which was synchronously detected using a PAR model 124 lock-in detector with an PAR model 116 preamplifier. The lock-in output was then read with a Keithley model 177 digital multimeter or recorded via a Hewlett-Packard model 7015B x-y recorder. This modulation technique made measurements very much less susceptible to interference from stray light. Laser power measurements were made using an Eppley thermopile. The system response was routinely checked for linearity using neutral-density filters.

To simulate a situation similar to one that may be encountered in an actual inspection scenario, the laser beam was directed onto the sample at an angle almost perpendicular to the surface (10° from the normal). The subsequent fluorescent light was collected from a solid angle normal to the sample surface and through an aperture plate placed in contact with the sample. The aperture diameter was 0.25 in. The samples were at standard room temperature; no measurements were attempted at extreme temperatures.

2. Reflectance

Because the physics of fluorescence and reflectance are both influenced by excited-electronic-state transitions, the effects are somewhat related. A Perkin-Elmer Lambda-9 Spectrophotometer with a 60-mm integrating-sphere reflectance attachment was used to make reflectance (as a function of wavelength) measurements on some of the samples. Because the aging seemed to mostly affect the "red" region of the spectrum, further measurements on all the samples were conducted using a portable Minolta Chroma Meter II. That instrument yielded the color readings in the standard "Yxy" chromaticity coordinates (1931 CIE standard color definitions using illumination "C"). The transformation $X=(x/y)Y$ was then used to yield the "X" tristimulus parameter which is a measure of "red" reflectance.

D. Data

1. Laser-Induced Fluorescence

a. Intensity as a Function of Age Intensity of the laser-induced fluorescence in arbitrary units (A.U.) is plotted as a function of the age (time immersed in 160°F water) in Figure 2A. This figure shows the data for four samples: Uniroyal "A" (UA), Uniroyal "B" (UB), Uniroyal "C" (UC), and Goodyear Coating (G). These data were taken with an excitation wavelength of 488 nm and a detection wavelength of 577 nm. It is apparent that laser-induced-fluorescence intensity increased as the material aged. With other excitation and detection wavelengths, these correlations were sometimes absent or of the opposite sign; for instance, with UB material (325-nm excitation and 400-nm detection), the laser-induced fluorescence of the aged material decreased when compared to the unaged. Additional representative data are shown in Figures 2B-2F. Standard deviations as percentages of the mean for each data point were typically 3%.

COMMENT ON TERMINOLOGY: Arbitrary units are used because the measured value of laser-induced fluorescence depends on the collection optics, detector response, and laser power density; therefore, the actual units have meaning only if all the other relevant parameters are specified. We have used the

convention that all data displayed on the same graph or table were recorded under constant experimental parameters.

Measurements were also conducted on samples that were artificially aged in a weatherometer. Similar graphs were obtained using those samples as shown in Figures 3A-3C; note that detailed behavior of the graphs depends on the method of artificial aging as apparent by comparison of general shapes of Figures 2A and 3A. (Note that numerical values of the laser-induced fluorescence intensity should not be literally compared between these two figures, since the experimental parameters mentioned above were slightly different.) The relationship between aging in hot water and aging in a weatherometer has not been established.

A few of the samples that had been aged in hot water were also subjected to ultraviolet radiation using the weathering tester at SwRI. Data from these samples are presented in Table II. Note that these data indicate that fluorophores are photoinitiated by ultraviolet exposure for some samples, because the laser-induced fluorescence-intensity increased after ultraviolet exposure.

Experiments were conducted on various other samples. Generally, the correlation of material characteristics with age was very weak or nonexistent for some of the "black", "very dark", or "translucent" samples tested in this study. Representative data using ultraviolet excitation are shown in Figures 4A and 4B. To obtain data from the black samples, laser power density was increased approximately an order of magnitude over that used for the other materials. Additionally, data repeatability was not as good for the black samples, typically 25% for the standard deviation as a percentage of the mean.

b. Differentiation Optimization Figure 5 shows the relative laser-induced-fluorescence ratio as a function of excitation wavelength. These data were taken to determine the best excitation wavelength for good differentiation of aged material from unaged material. Data presented in Figure 5 were recorded using UB material which had been aged for 400 hours in a weatherometer or unaged. The two different samples were illuminated with various lasers. Detection wavelengths were then optimized for each excitation wavelength as shown in Table III. The ratio between the signal from aged material and the signal from unaged material was then plotted as a function of excitation wavelength. This graph can be interpreted to indicate that the best differentiation for UB material was obtained using 488-nm excitation (one of the argon-ion laser wavelengths). Other wavelengths can be used, but with a loss in differentiation ability. As an example, a helium-neon laser operating at 543.5 nm would yield a lower ratio.

c. Fluorescence Quenching Several other types of experiments were performed using selected available samples. If excitation power densities were too high, then fluorescence quenching would occur to some degree during the measurement. (This effect was discovered because the lasers available in our laboratory included a high-power laser capable of several-watt output concentrated in a 1.5-mm beam diameter.) The time constant (for laser-induced fluorescence from the material to decrease by a factor of two) was typically on the order of thirty minutes when a power density of 86 milliwatts per square centimeter was used to irradiate material UA. At that

power density, degradation was not noticeable to the naked eye. Typical illustrative data are shown in Figures 6A and 6B. This effect is of no concern in the present application, since a small low-power laser is desirable anyway, due to its portability; furthermore, the measurements will be performed on time scales on the order of seconds.

2. Reflectance

Standard reflectance measurements were also conducted on the samples. Typical data are shown in Figures 7A-7I. Notice that the detailed behavior of these graphs also depends on the method of aging, as can be seen by comparing Figure 7C with Figure 7G; however, as mentioned above, the relationship between aging in hot water and in the weatherometer has not yet been established. It was also noticed that visual appearances of the samples aged with various techniques were also different. For instance, the samples aged in hot water had a higher specular reflectivity than those aged in the weatherometer (i.e. the weatherometer samples were not as "shiny").

E. Results

1. Laser-Induced Fluorescence

Tensile-strength and elongation data supplied by Ft. Belvoir are shown in Figures 8A, 8B, 9A, and 9B. (Error bars were not supplied with these data; however, some estimation of uncertainty in the data can be made based on irregularities of the curves.) A strong correlation exists between the change in tensile strength (e.g., Figure 8A) and laser-induced-fluorescence intensity (e.g., Figure 2A) for many of the materials tested. Note that the G material does not undergo a significant tensile-strength change, and therefore a significant change in the laser-induced-fluorescence signal does not occur over the range of aging under study.

This strong correlation exists for only the right combination of excitation and detection wavelengths. Correlation exists because of the complex molecular and intermolecular relationships that are altered as the material ages. Generally, structural changes that induce rigidity tend to promote fluorescence, because internal vibrational relaxation (nonradiative) processes are minimized. By using excitation wavelengths longer than the primary absorption wavelengths in conjunction with low power densities, bleaching and photodegradation effects can be avoided because the photon energies are not enough to break most chemical bonds. Additionally, choice of excitation wavelength is somewhat influenced by impurities in the polymer; that is to say, if a certain excitation wavelength, causes impurities in the polymer to fluoresce strongly, then that would not be a suitable choice. (For example, the strong ultraviolet-excited fluorescence of scavenger additives can be avoided.)

2. Reflectance

The difference in reflectance between aged and unaged samples was very much less than the corresponding change in the laser-induced fluorescence as is shown in Table IV. A technique based on laser-induced fluorescence will be much more sensitive to aging than one based on reflectance because of these differences.

3. Discussion

A major question with the present work is how the artificially aged materials compare with actual items that have been aged in natural ways. Additionally, there is some question in how different aging methods affect laser-induced-fluorescence signals. For instance, the amount and wavelength of ultraviolet exposure will have some effect on the differentiation capability of the laser-induced-fluorescence technique because of the ultraviolet photoinitiation of fluorophores.

III. INTEGRATED FLUORESCENCE AND OPTIMIZATION EXPERIMENTS

A. Introduction

The work described above has been based on the laser-induced-fluorescence intensity for a particular detection wavelength. For a low-cost portable field unit, it would be advantageous to replace the spectrometer system with a simple optical filter and low-cost detector. Detail spectral characteristics of laser-induced-fluorescence intensity and detector response determine whether or not this can be done. We have conducted several experiments to establish this feasibility.

When the spectrometer system was replaced with optical filters, fluorescence signals of several wavelengths were measured simultaneously. Laser-induced fluorescence measured in this fashion is referred to as "integrated fluorescence" because the signal is related to the integral of the fluorescent-light intensity, weighted by the filter-detector response, over the wavelengths to which the system responds. Hence

$$I(\lambda_e) = \int LIF(\lambda) D(\lambda) f(\lambda) d\lambda \quad [\text{Eq. 1}]$$

where

$I(\lambda_e)$ = integrated fluorescence for excitation wavelength λ_e

$LIF(\lambda)$ = laser-induced fluorescence as a function of wavelength λ

$D(\lambda)$ = detector response as a function of wavelength λ

$f(\lambda)$ = filter response as a function of wavelength λ .

This "integrated fluorescence" can always be measured; however, the question of importance is whether the capability of differentiation of the degree of degradation exists as it does with single-wavelength fluorescence.

B. Samples

Materials UA, UB, UC, and G (aged in hot water) supplied by the Ft. Belvoir Research, Development and Engineering Center were used in the following work. (See Table I for material descriptions.)

C. Equipment and Procedures

Experimental apparatus for measuring integrated fluorescence is shown in Figure 10. An unfocussed, modulated laser beam with a power of several milliwatts or less was directed at the sample. The subsequent reflected and fluorescent light was filtered through Schott glass filters and imaged with a short-focal-length (19-mm) lens onto a United Detector Technologies (UDT) model PIN-10 Schottky-barrier silicon photodiode (0.3-1.1 μm response) operated in the photoconductive mode (-9 V reverse bias and a

100-k Ω load resistor). The angle between the laser beam and the detection optics was approximately 30°. The distance from the sample to the detection filter was approximately 50 mm. The detection electronics consisted of a Princeton Applied Research (PAR) model 124/116 lock-in amplifier with the output monitored with a Keithley model 177 digital multimeter. A reference signal (approximately 2.0 kHz) for the lock-in detection was supplied from a PAR model 125A mechanical light chopper that modulated the laser beam.

D. Data

1. Integrated Fluorescence

Using the UA, UB, UC and G samples that were aged in hot water, integrated fluorescence data were obtained for two excitation wavelengths, 488 nm (from an argon-ion laser) and 543.5 nm (from a helium-cadmium laser). These wavelengths were chosen because they represent two leading candidates for small portable laser systems. The filter used was a 6-mm-thick Schott OG570. For both excitation wavelengths, integrated-fluorescence data were very similar to the single-wavelength fluorescence data. Only very minor differences existed in the differentiation between unaged and degraded materials.

2. Polarization

While using an unpolarized excitation laser no fluorescence polarization was observed; however, when using a linearly polarized laser, a 6% or less difference was measured between the two possible polarization orientations for fluorescence. This may have been related to reflection losses from the semi-glossy surface.

3. Filter Optimization

While using the integrated-fluorescence technique, optimization of the filter-detector combination was investigated. With the set-up as shown in Figure 10, 543.5-nm excitation and the UDT PIN-10 detector, a better differentiability resulted for the UB material by using an OG630 filter, although the absolute signal strength was slightly decreased (see Figure 11A). The differentiability was better by a factor of approximately 1.3.

4. Lock-in Mode Versus AC-Voltmeter Mode

Detection electronics were operated in either the phase-sensitive lock-in mode or the ac-voltmeter mode. The advantage of the ac-voltmeter mode was that the phase-shift between the reference signal and the fluorescence did not have to be set. However, in this mode interference from room light was somewhat more troublesome, and led to an offset in the readings. For example, using a frequency of 2.0 kHz and a quality factor Q of 10, the following signal voltages were recorded with the room lights off: 5.20 V (lock-in mode) and 5.15 V (ac-voltmeter mode). On the other hand, with the room lights on, corresponding voltages were as follows: 5.21 V (lock-in mode) and 8.80 V (ac-voltmeter mode). True fluorescence should have yielded the same value with room lights either on or off; therefore, for a field unit the lock-in detection mode would have an advantage.

5. Backing Material

Because the samples were not completely opaque, some experimentation was conducted to determine the influence of the material behind the 0.05-in. thick elastomer samples. Black vinyl tape was used as a nearly complete absorber, a mirror was used as a reflector, and several layers of polyurethane were used for intermediate values of reflectance. While using aged UB material, fluorescence was measured with 543.5-nm excitation, and the standard deviation for all the measurements was 1.2% of the mean. As expected, fluorescence was very slightly higher using the mirror as a backing and very slightly lower using the black tape; thus, the backing material has only a minor influence on fluorescence measurements, for these samples.

6. Reflectance/Integrated-Fluorescence Ratio

To determine approximately how much of the incident light was converted to fluorescent light as compared to reflected light, experiments were conducted using the apparatus of Figure 10. With 543.5-nm excitation and an RG630 filter, integrated fluorescence was measured. When the RG630 filter was removed, the signal was then mainly due to the reflected light, because reflection and absorption dominate fluorescence in "nonfluorescent" materials. The spectral response of the silicon photodiode was not taken into account for this measurement, because it was only approximately a 20% effect over the wavelength region under consideration. The ratio of reflected light to fluorescence was obviously a function of the state of degradation and the material, but it did give an order-of-magnitude for the effect. For UB aged in a weatherometer for 400 hours (UB400), the ratio was

$$\frac{\text{Reflectance UB400 (543.5 nm)}}{\text{Integrated Fluorescence UB400 (543.5 nm excitation/RG630 detection)}} = 137$$

However, for unaged samples of the same material, the ratio was

$$\frac{\text{Reflectance UB0 (543.5 nm)}}{\text{Integrated Fluorescence UB0 (543.5 nm excitation/RG630 detection)}} = 2648.$$

Therefore, the integrated fluorescence was approximately 0.03% as intense as the reflected light for unaged UB material, but increased to almost 1% for aged UB material.

E. Results

The work described above indicates that the capability of differentiation between degraded and nondegraded samples does exist using the "integrated fluorescence" technique.

IV. BIFURCATED FIBER-OPTIC BUNDLE EXPERIMENTS

A. Introduction

Because the integrated-fluorescence measurements proved successful, the next step to prove concept feasibility was to construct and test a laboratory "breadboard" assembly.

B. Samples

The samples used to test the "breadboard" assembly were UA, UB, UC, and G (aged in hot water) supplied by the Ft. Belvoir Research, Development and Engineering Center. (See Table I for material descriptions.)

C. Equipment and Procedures

Experimental apparatus for measuring laser-induced fluorescence through a bifurcated (two-channel) fiber-optic bundle is shown in Figure 12. Typical experimental parameters were as follows:

Laser:	Argon-ion, 488 nm, power 0.5 mW measured at input to fiber (after the interference filter and modulator),
Modulator:	PAR model 125A mechanical chopper, 2.0 kHz,
Filter F1:	Interference filter @ 488 nm, Edmund P/N 030907,
Fiber:	Oriel P/N 77533, 36 in. bifurcated bundle, diameter at junction end 0.177 in., bundle diameter at input/output ends 0.125 in., numerical aperture (NA) = 0.55, material: glass, average loss over visible wavelength region: 45%, stand-off distance "d" from sample: 22mm,
Filter F2:	Schott OG570, 2 each, 3.0-mm thick,
Detector:	UDT PIN-10 Schottky-barrier silicon photodiode operated in the photoconductive mode (-9 V bias, 100-k Ω load resistor), a 19-mm-focal-length lens (36 mm from the detector) imaged the output from the bundle (44 mm from lens) onto the detector,
Electronics:	PAR model 124 lock-in amplifier with a model 116 preamplifier, sensitivity: 10 μ V scale, quality factor Q = 10 at 2.0 kHz, time constant 300 ms, monitored with a Keithley model 177 digital multimeter.

No lenses were used to image the laser beam into the bundle because the bundle diameter was larger than the diameter of the laser beam. This did result, however, in an output beam diameter (18 mm at the sample) of slightly less than that which could have been theoretically obtained (28 mm at the sample) if input optics had been used.

D. Data

1. Stand-off Distance

The stand-off distance, "d" in Figure 12, from the end of the fiber bundle to the sample was an important parameter. Fluorescent light emanated from the sample in all directions from the point that the laser beam hit the surface. When the stand-off distance was large, not as much fluorescent light was collected by the bundle and subsequently analyzed;

therefore, when comparing different samples, care had to be taken to make sure that the stand-off distance was constant. Additionally, slight deviations were noticed in differentiability when various stand-off distances were used.

2. Interference Filters

The OG570 Schott glass filter was replaced with a narrow-band (10-nm) interference filter with the central wavelength at 580 nm (Oriel P/N 54390). The signal strength was very much less, because only one small band of wavelengths contributed to the measurement. The signal-to-noise ratio was much worse, and no quantitative measurements were attempted. This demonstrated the advantage of using the integrated-fluorescence technique.

3. Filter Optimization

While using integrated-fluorescence through the fiber-optic bundle, optimization of the filter-detector combination was also investigated. With the set-up shown in Figure 12, 488-nm excitation and the UDT PIN-10 detector, a better differentiability resulted for the UB material by using an OG630 filter, but the absolute signal strength was decreased by about a factor of 2.5 (see Figure 11B) while differentiability was better by a factor of approximately 2. This work implies that some accommodation for changing filters may be advantageous for a field unit.

4. Concept Demonstration

The fiber-optic bundle set-up of Figure 12 was used with the experimental parameters listed above to measure laser-induced fluorescence as a function of sample age for several elastomers. (See Figures 13A-13B.) Standard deviations for each data point were typically 3% of the mean. For future reference it should be noted that the y-axis units (labelled as arbitrary units) of Figures 13A and 13B were actually volts where 10 volts corresponded to full-scale of the lock-in amplifier (operated on the 10- μ V-full-scale range).

5. Linearity

Linearity of laser-induced-fluorescence intensity as a function of laser power density was investigated. For power densities below 20 milliwatts per square centimeter, laser-induced-fluorescence intensity was linearly related to the laser power density. (This is probably true at higher power densities; however, no measurements were made above that power-density regime in order to avoid fluorescence-quenching effects, if any.) Figure 14 shows a log-log presentation of laser-induced fluorescence as a function of laser power for three different ages of UB material. (The displayed straight lines are for ease of viewing.) Notice that the curves remain linear as the material degrades even though the total signal increases. The three curves displayed in Figure 14 were fitted with the best linear-least-squares analysis and the slopes deviated less than 3% from unity with linear correlation coefficients better than 0.999.

6. Correlation of Laser-Induced Fluorescence with Tensile Strength

Typical scatter diagrams which relate laser-induced fluorescence to tensile strength are shown in Figures 15A-15D. A strong correlation exists for UA, UB, and UC materials. (Fluorescence data were measured through the fiber-optic bundle, with 488-nm excitation, and integrated-fluorescence detection accomplished with a OG570/PIN diode-detector combination.) Correlation can be approximated by a linear function for each material if the data point from the unaged sample (highest tensile strength) is not considered; this type of very rapid initial degradation has been observed by other researchers [Ref. 13]. Correlation from the nitrile G samples is not strong over the range investigated, because the material has just started to degrade. The two data points shown in Figures 15D and 15E for material G are from the most aged samples (42 and 70 days in hot water) with the dotted line shown for ease of viewing.

It can be seen from these scatter diagrams that for the UA material, correlation may be slightly better described by a nonlinear function or combinations of functions; however for comparison purposes, a linear-least-squares analysis has been used for all three materials UA, UB, and UC, linear-correlation coefficients being $-.895$, $-.990$, and $-.940$, respectively. Notice that the slopes (laser-induced-fluorescence change for the same geometrical/experimental set-up per unit change in tensile strength) are different (-0.00167 , -0.00389 , and -0.00208 , respectively). This indicates that a different correlation relationship exists for each type of material.

E. Results

These data demonstrate that the method of "integrated fluorescence" can be used through a fiber-optic bundle to differentiate the degree of degradation of elastomers. Small, relatively low-cost equipment can be used for the measurements. For certain materials, a very high degree of correlation exists between laser-induced fluorescence and tensile strength.

In some cases, the integrated-fluorescence through the fiber-optic bundle renders more of an increase in signal as a function of age than does the single-wavelength method. For example, compare the data from the G material, single-wavelength detection (Figure 2B) with that of the integrated-fluorescence through the fiber-optic bundle (Figure 13B).

V. CONCLUSIONS AND RECOMMENDATIONS

Highlights of this work can be reviewed by following one group of samples (e.g., UA, UB, UC, and G aged in hot water) through the progression of experiments:

1. Laser-induced fluorescence with single-wavelength excitation and single-wavelength-fluorescence detection (Figure 2A),
2. Tensile-strength measurements (Figure 8A),
3. Laser-induced fluorescence with single-wavelength excitation and integrated-fluorescence detection through a fiber-optic bundle (Figure 13A),
4. Correlation analysis of laser-induced fluorescence (integrated fluorescence measured through a fiber-optic bundle) as a function of tensile strength (Figures 15A-15E),
5. Conceptual diagram for implementation of a field unit (Figure 16).

Correlation between laser-induced fluorescence and material degradation exists for many of the materials tested because of the complex molecular and intermolecular relationships (such as cross-linking, scission, oxidation) that are altered during degradation. Intensity of laser-induced fluorescence is promoted because of the decrease of internal relaxation processes when degradation modifies these relationships.

Because the excitation photon energies are not high enough to break most chemical bonds or excite fluorescence from most of the impurities, many complications normally associated with fluorescence measurements can be avoided.

The conceptual diagram for a developmental prototype, shown in Figure 16, is based on a low-power laser (a few milliwatts) with a fiber-optic bundle to deliver the laser beam and collect fluorescent light. Further design details are described in SwRI Proposal 15-3363B.

Advantages of an inspection device based on these principles:

- * Nondestructive
- * Portable
- * Easy to use (Material requires minimal preparation)
- * Fast (Very little time needed for signal averaging)
- * Versatile (May work for a variety of materials).

Disadvantages of the technique:

- * Somewhat limited in application (Correlation of laser-induced fluorescence with tensile strength is not good for some "black" materials)
- * Must be calibrated for each type of material
- * May be somewhat sensitive to stray light (Dependent on detection method used).

The work described above demonstrates that practical application of the laser-induced fluorescence inspection technique to polyurethanes and other elastomers is very promising, and further development should be conducted.

VI. REFERENCES

A. Footnotes

1. Encyclopedia of Polymer Science and Engineering, John Wiley and Sons, Wiley-Interscience, (New York, NY) 1986, Vol. 4, pp 630-693, Vol. 6, pp. 636-638.
2. "Polymer Photophysics," J. M. Torkelson, *Physics Today*, pp. S-64 (Jan. 1987).
3. Instrumental Methods of Analysis, H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, 4th Ed., Van Nostrand Reinhold Co., (New York, NY) 1948, p. 85.
4. "Effect of Polymer Chain Tacticity on the Fluorescence of Molecular Rotors," R. O. Loutfy and D. M. Teegarden, *Macromolecules* **16**, pp. 452-456 (1983).
5. "Photochemical Reactions in an MDI-Based Elastomeric Polyurethane," N. S. Allen and J. F. McKellar, *J. of Appl. Polymer Sci.* **20**, pp. 1441-1447 (1976).
6. "Novel Excimer Fluorescence Method for Monitoring Polymerization," F. W. Wang, R. E. Lowry, and W. H. Grant, *Polymer* **25**, pp. 690-692 (1984).
7. "A Study of Polymers Using Fluorescent Dyes," C. A. Byrne, E. J. Poziomek, O. I. Kutai, S. L. Suib and S. J. Huang, in Materials Characterization for Systems Performance and Reliability, (Proceedings of the Sagamore Army Materials Research Conference: 1984) Ed. by J. W. McCauley and V. Weiss, Plenum Press (New York, NY) 1986, pp. 495-503.
8. "Fluorescence in Polymers," C. A. Byrne, E. J. Poziomek, O. I. Kutai, S. L. Suib, and S. J. Huang in Polymers as Biomaterials, Ed. by S. W. Shalaby, A. S. Hoffman, B. D. Ratner, and T. A. Horbett, Plenum Press (New York, NY), 1985, pp. 111-120.
9. "Fluorescence Probes for Solid Polymer Films," R.O. Loutfy, *SPIE 743: Fluorescence Detection*, Ed. by E. R. Menzel, p. 54-59, (1987).
10. "Cure Monitoring of Epoxy Resins by Fluorescent Spectroscopy," F.W. Wang, R.E. Lowry and B.M. Fanconi, *Polymeric Materials Science and Engineering*, **53**, pp. 180-185, (1985).
11. "Cure Monitoring of Epoxy Resins by Fluorescence Recovery After Photobleaching," F.W. Wang and E. Wu, *Polymer Commun.* **28**, pp. 73-75, (1987).

12. "Pex Scanner, A New Instrument to Measure On-Line the Degree of Cross-Linking in Polyethylene Plastics," M. Luukkala and J. Viirto, J. of Indust. Irradiation Tech 2 (3,4), pp. 353-366, (1984).
13. Reference 7, p. 498.

B. Bibliography

1. Polyurethane Elastomers, C. Hepburn, Applied Science Publishers, London and N.Y., (Elsevier Science Publishing, NY) 1982.
2. Rubber Technology, 2nd Edition, Edited by Maurice Marton, (Van Nostrand Reinhold Co., NY) 1973.
3. Plastics Materials, 4th Edition, J.A. Brydson, (Butterworth Scientific, London, Boston) 1982.
4. Additives for Plastics, J. Stepek and H. Daoust (Springer-Verlag, NY) 1983.
5. Color Science, Gunter Wyszecki and W.S. Stiles (John Wiley & Sons, Inc., NY) 1967.
6. Fluorescence and Phosphorescence, Peter Pringsheim, (Interscience Publishers, NY) 1949.
7. The Physics and Chemistry of Color, Kurt Nassau, (John Wiley and Sons, NY) 1983.

VII. TABLES AND FIGURES

TABLE I. SAMPLES

Code	Manufacturer	Description	Color *	Thickness (in.)	H	W	UV
UA	Uniroyal	ester-based PU	amber	0.05	X	X	X
UB	Uniroyal	ester-based PU	amber	0.05	X	X	X
UC	Uniroyal	ether-based PU	amber	0.05	X	X	X
G	Goodyear	coating, nitrile	amber	0.075	X	X	
GF	Goodyear	fabric, nitrile	amber	0.075		X	
PU1	Ft. Belvoir	carbon/ester-based PU	black	0.075	X	X	
PU1S	Ft. Belvoir	silica/ester-based PU	dk brwn	0.075	X	X	
PU2	Ft. Belvoir	carbon/ether-based PU	black	0.075	X	X	
PU2S	Ft. Belvoir	silica/ether-based PU	black	0.075	X	X	
EST	Goodrich	Estane 5708 PU	lt amber	0.075	**		
LU1	Lord	castable PU	transluc	0.1	**		
LU2	Lord	castable PU	transluc	0.075	**		
LU3	Lord	castable PU	transluc	0.1			
LU4	Lord	castable PU	transluc	0.1			
LU5	Lord	castable PU	transluc	0.1			
CD	Disogrin	9250 high temp PU	yl white	0.075			

* = Nominal color of unaged material

**= Hot-water temperatures and aging times differed from other samples.

H = Hot-water aging at 160°F ranging to 70 days.

W = Weatherometer aging in 160°F with intermittent water spray and ultraviolet exposure ranging to 500 hours.

UV= Samples that had been aged for 28 days in 160°F water were additionally exposed to ultraviolet for 120 hours.

Table II. FLUOROPHORE PHOTOINITIATION IN POLYURETHANE

Sample	LIF Ratio (QUV/no QUV) *
UA (28 Days in 160 F Water)	1.0
UB (28 Days in 160 F Water)	2.3
UC (28 Days in 160 F Water)	5.3

* Note: QUV= 120 hours in a QUV Weathering Tester without water (313 nm peak, 280 nm low cut-off). Excitation wavelength 488 nm, detection wavelength 577 nm.

TABLE III. DIFFERENTIATION OPTIMIZATION WAVELENGTHS (Samples: UB(400 hrs) and UB(unaged); Aging Method: Weatherometer)

Excitation Wavelength (nm)	Detection Wavelength (nm)
351.1+363.8	560
457.9	577
488	577
514.5	577
543.5	593
632.8	671

TABLE IV. COMPARISON OF THE LASER-INDUCED-FLUORESCENCE AND REFLECTANCE METHODS FOR DETERMINATION OF AGING (Aging method: Hot Water)

Sample	Tristimulus Value Ratio ¹	Laser-Induced Fluorescence Ratio ²
UA	1.54	184.
UB	1.76	209.
UC	1.26	25.5
G	1.05	1.33

1. $X(0 \text{ days})/X(70 \text{ days})$ where X is the X tristimulus parameter.

2. $LIF(70 \text{ days})/LIF(0 \text{ days})$ where LIF is the laser-induced-fluorescence intensity using 488 nm excitation and 577 nm detection.

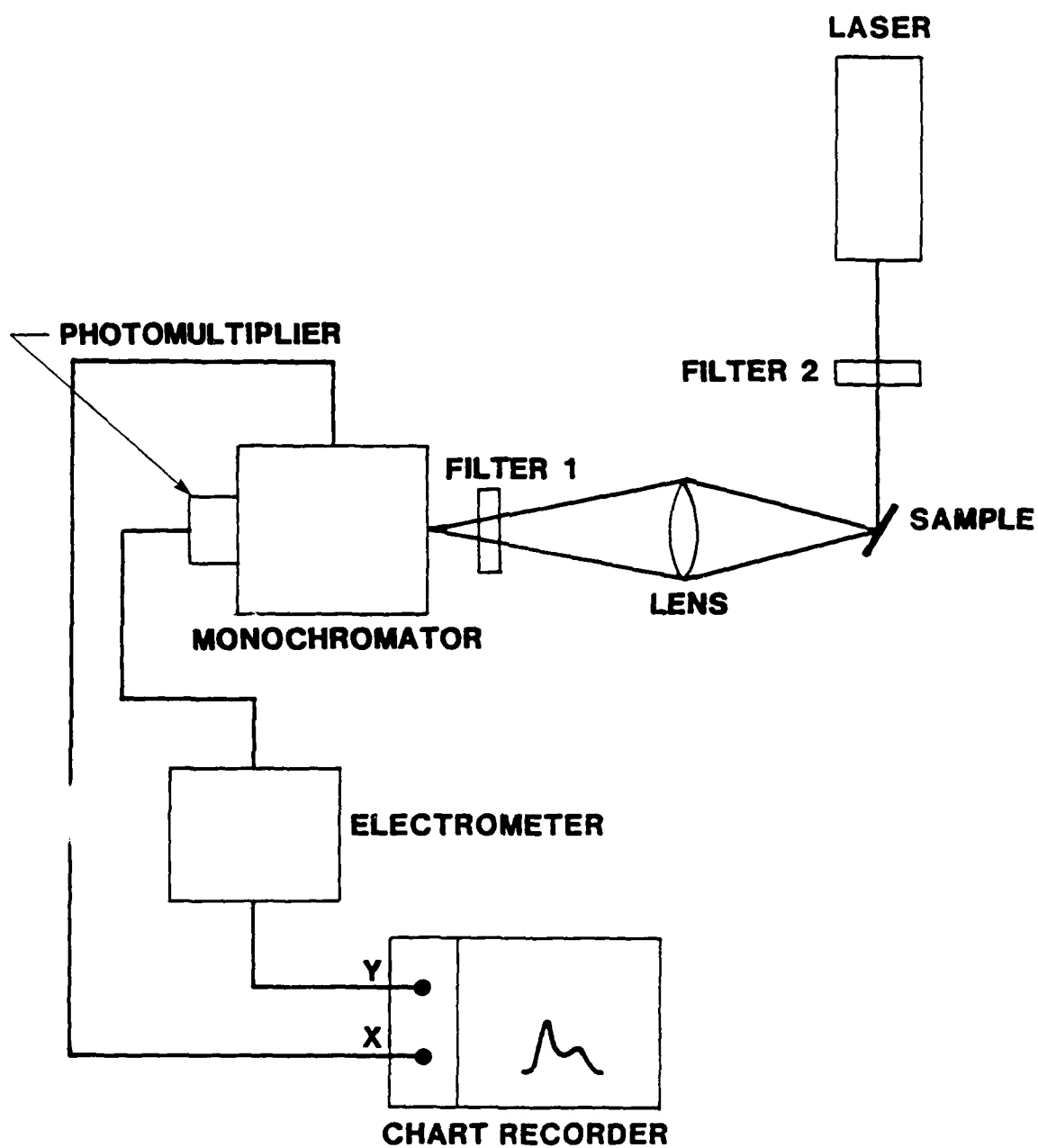


FIGURE 1. EXPERIMENTAL APPARATUS FOR BASIC RESEARCH UTILIZING LASER-INDUCED FLUORESCENCE

LIF DATA (UA=1,UB=2,UC=3,G=4)
(EXCITATION=488NM DETECTION=577NM)

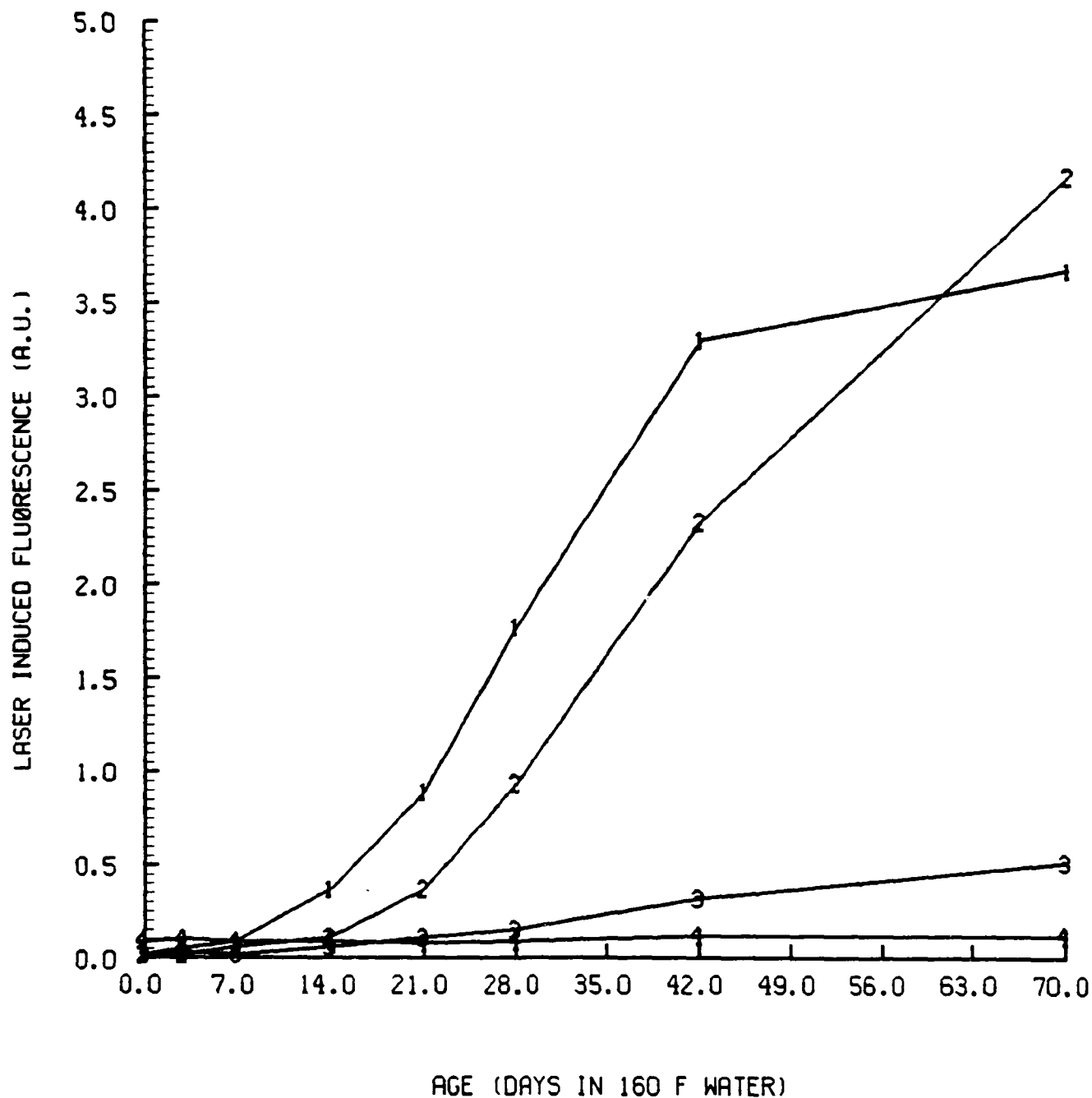


FIGURE 2A. LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE
(Ex: 488 nm; Det: 577 nm; Samples: UA, UB, UC, G; Aging Method: Hot Water)

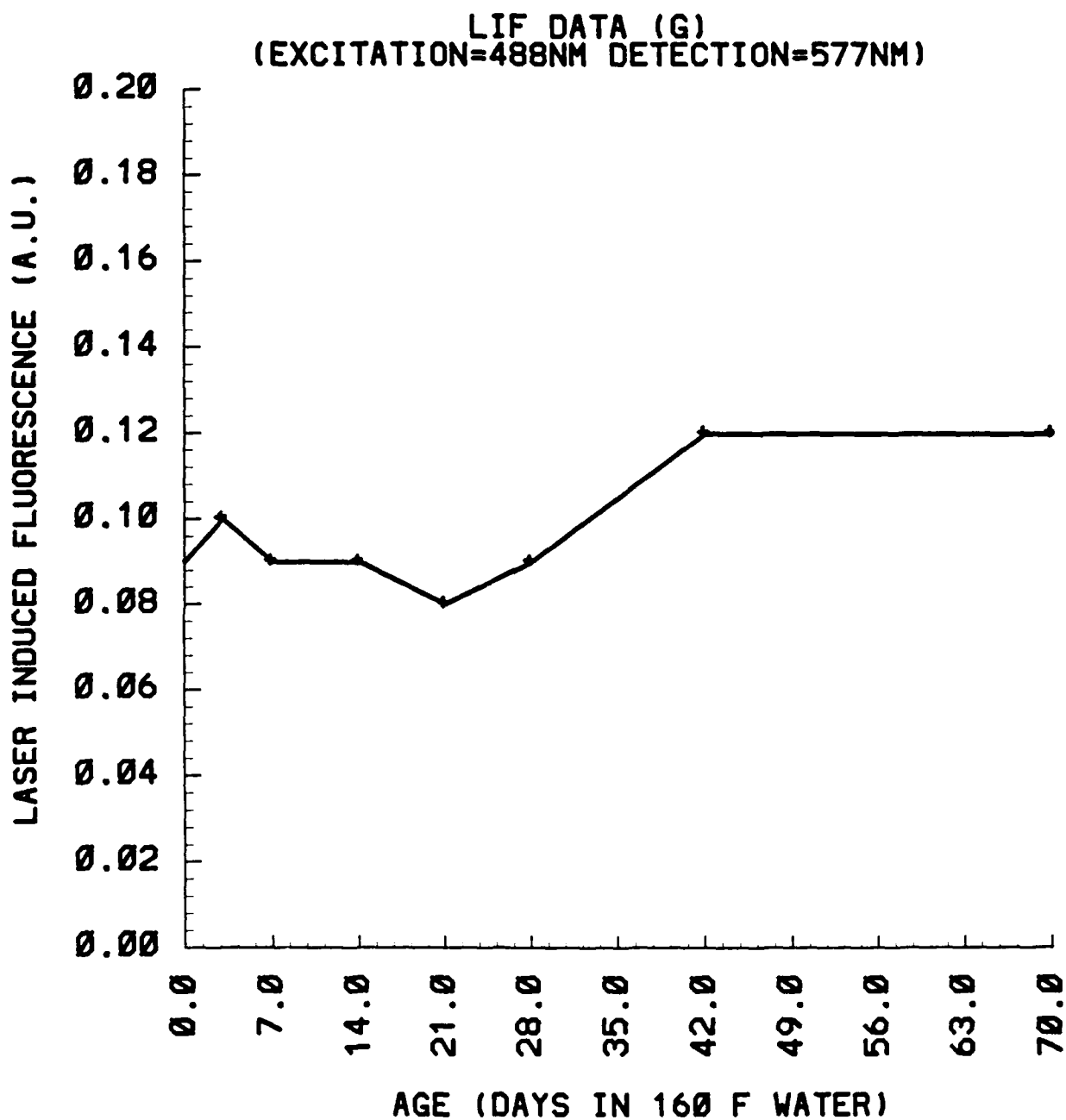


FIGURE 2B. LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE
(Ex: 488 nm, Det: 577 nm, Samples: G; Aging Method: Hot Water; Comments:
Expanded scale of Figure 2A)

LIF DATA (PU1=1, PU2=2, PU1S=3, PU2S=4)
(EXCITATION=488NM DETECTION=577NM)

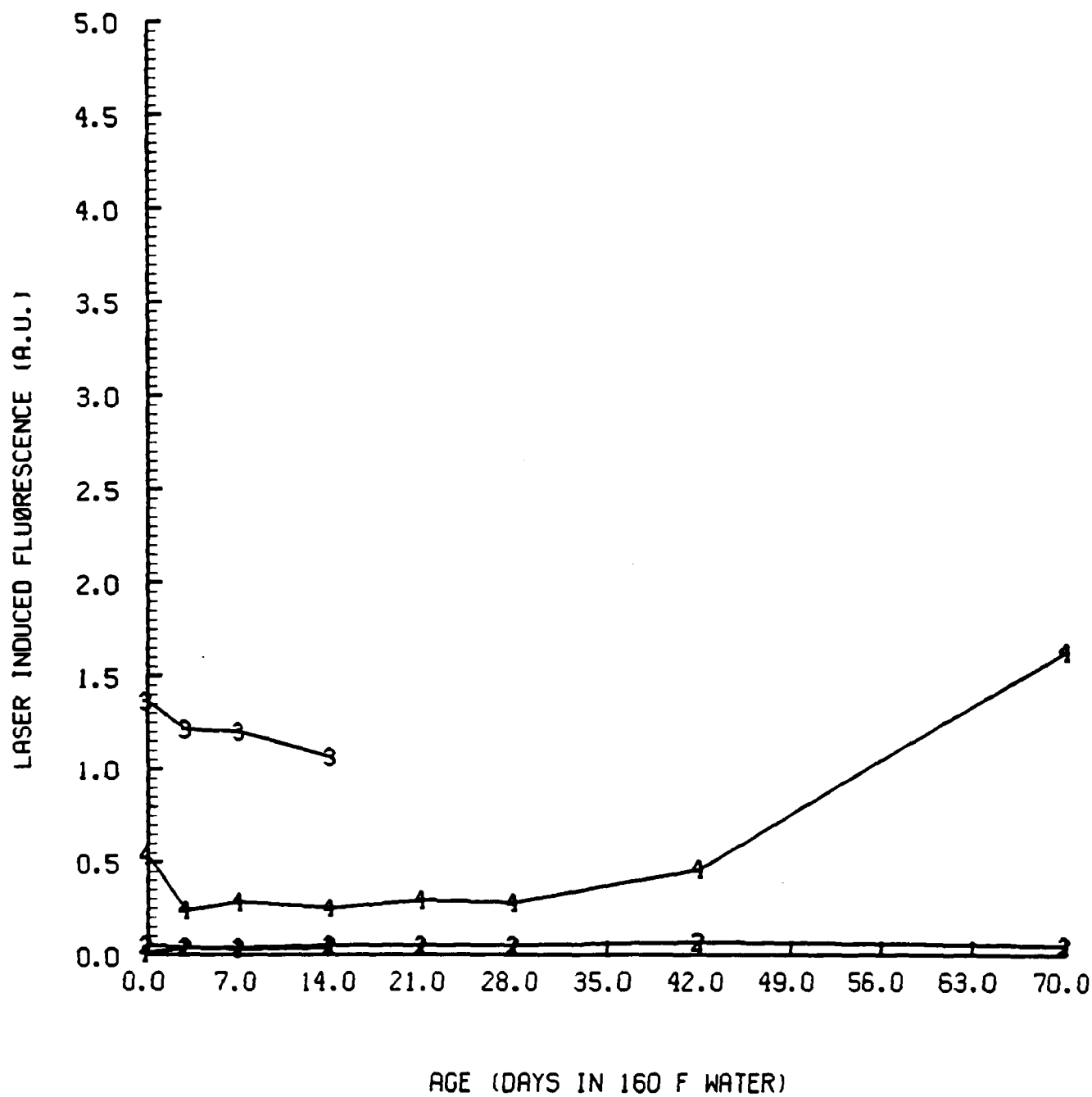


FIGURE 2C. LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE
(Ex: 488 nm; Det: 577 nm; Samples: PU1, PU2, PU1S, PU2S; Aging Method:
Hot Water)

LIF DATA (PU1=1, PU2=2)
(EXCITATION=488NM DETECTION=577NM)

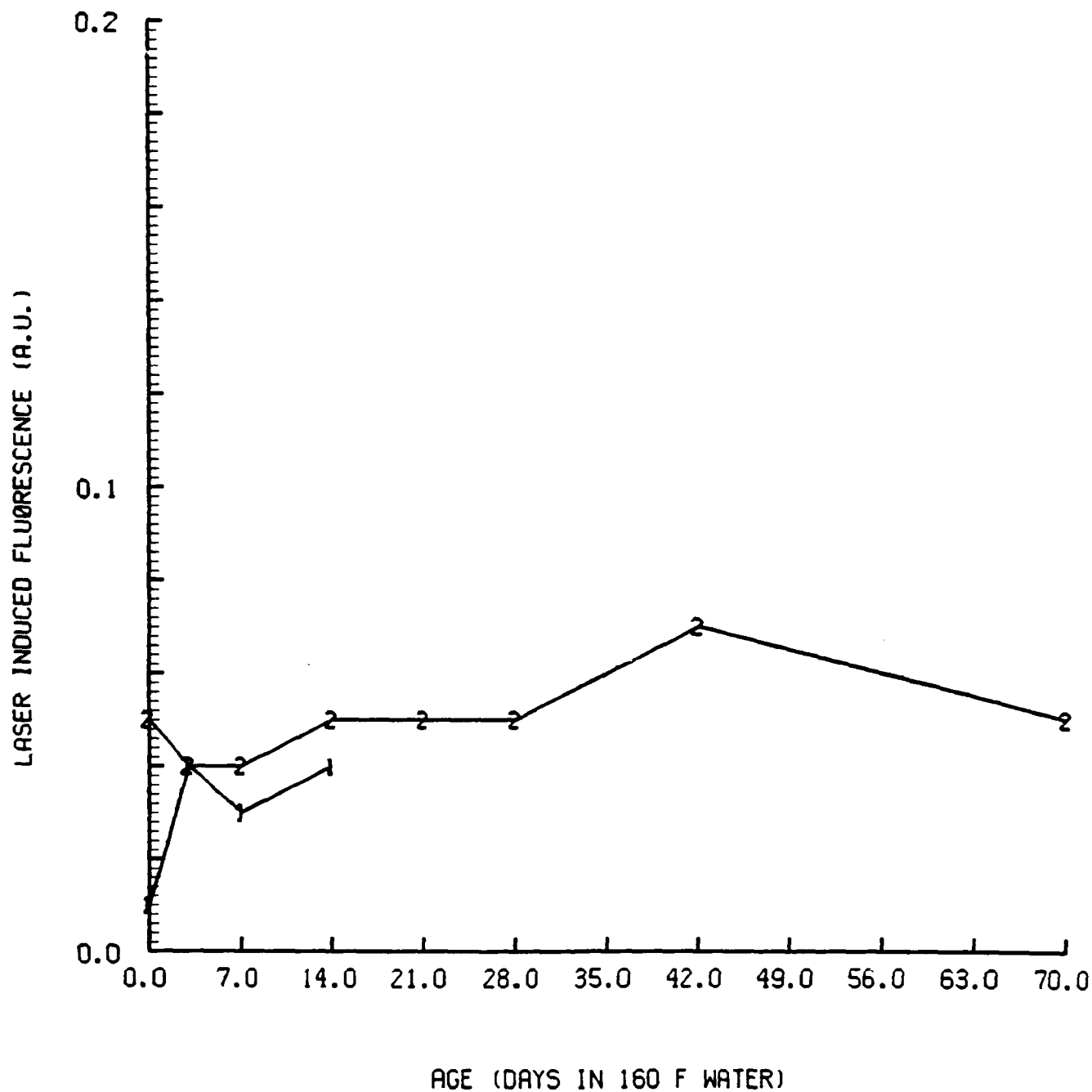


FIGURE 2D. LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE
(Ex: 488 nm; Det: 577 nm; Samples: PU1, PU2; Aging Method: Hot water;
Comments: Expanded scale of Figure 2C)

LIF DATA ON ESTANE 5708
(EXCITATION=488NM DETECTION=577NM)

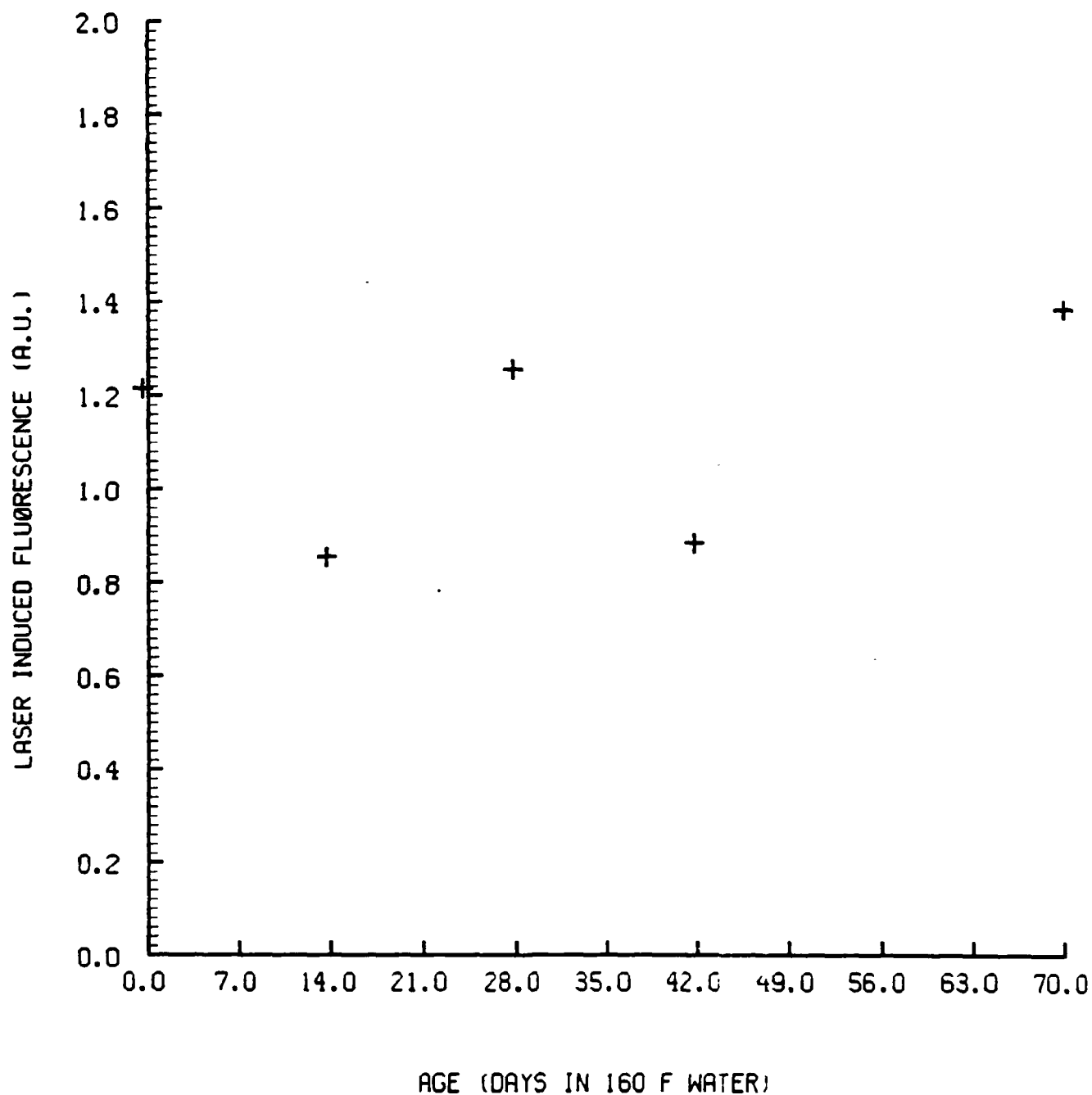


FIGURE 2E. LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE
(Ex: 488 nm; Det: 577 nm; Samples: EST; Aging Method: Hot water)

LIF DATA (LU1=1, LU2=2)
(EXCITATION=488NM DETECTION=577NM)

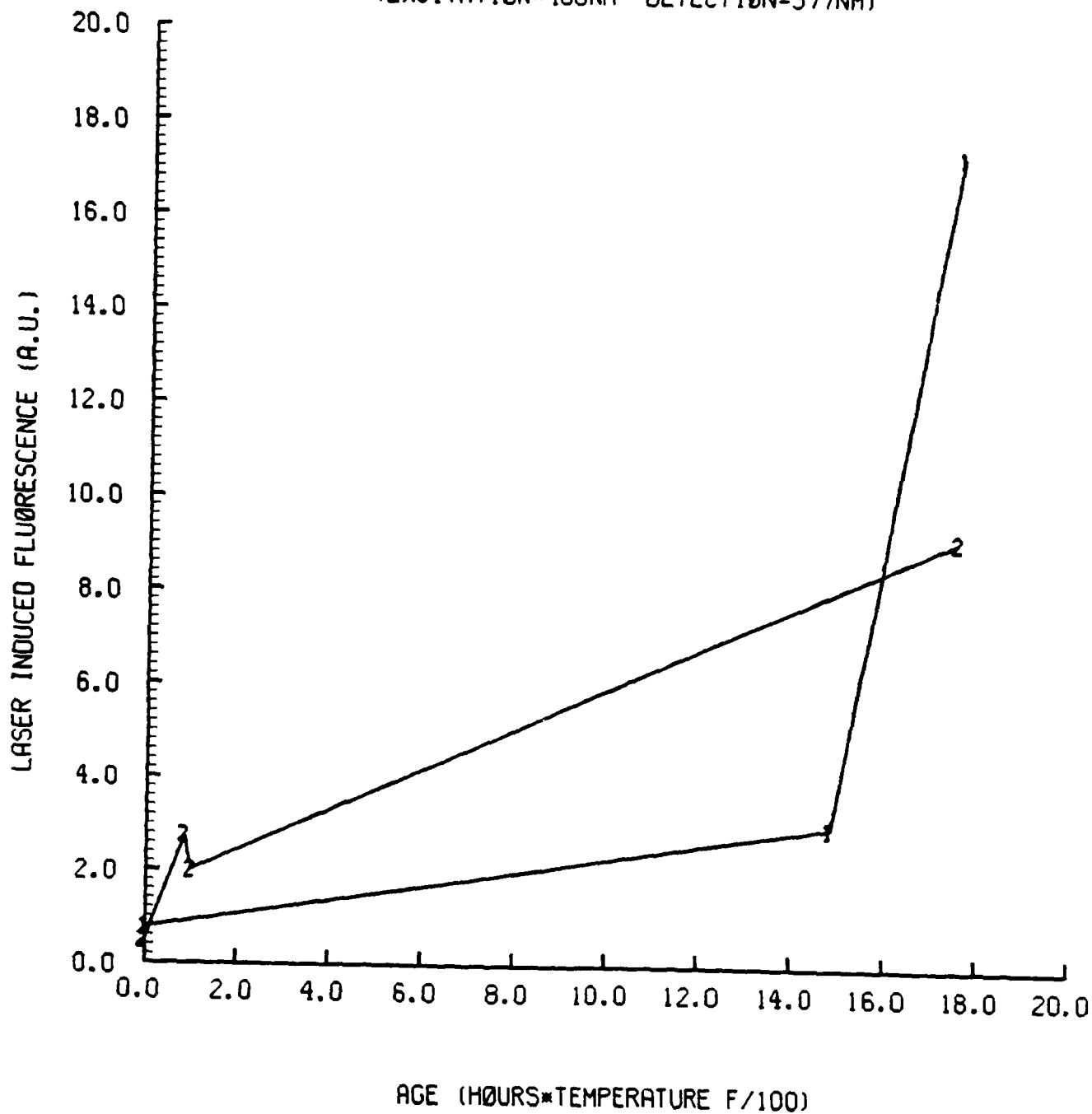


FIGURE 2F. LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE
(Ex: 488 nm; Det: 577 nm; Samples: LU1, LU2; Aging Method: Hot water;
Comments: Note that age coordinate slightly differs from other graphs)

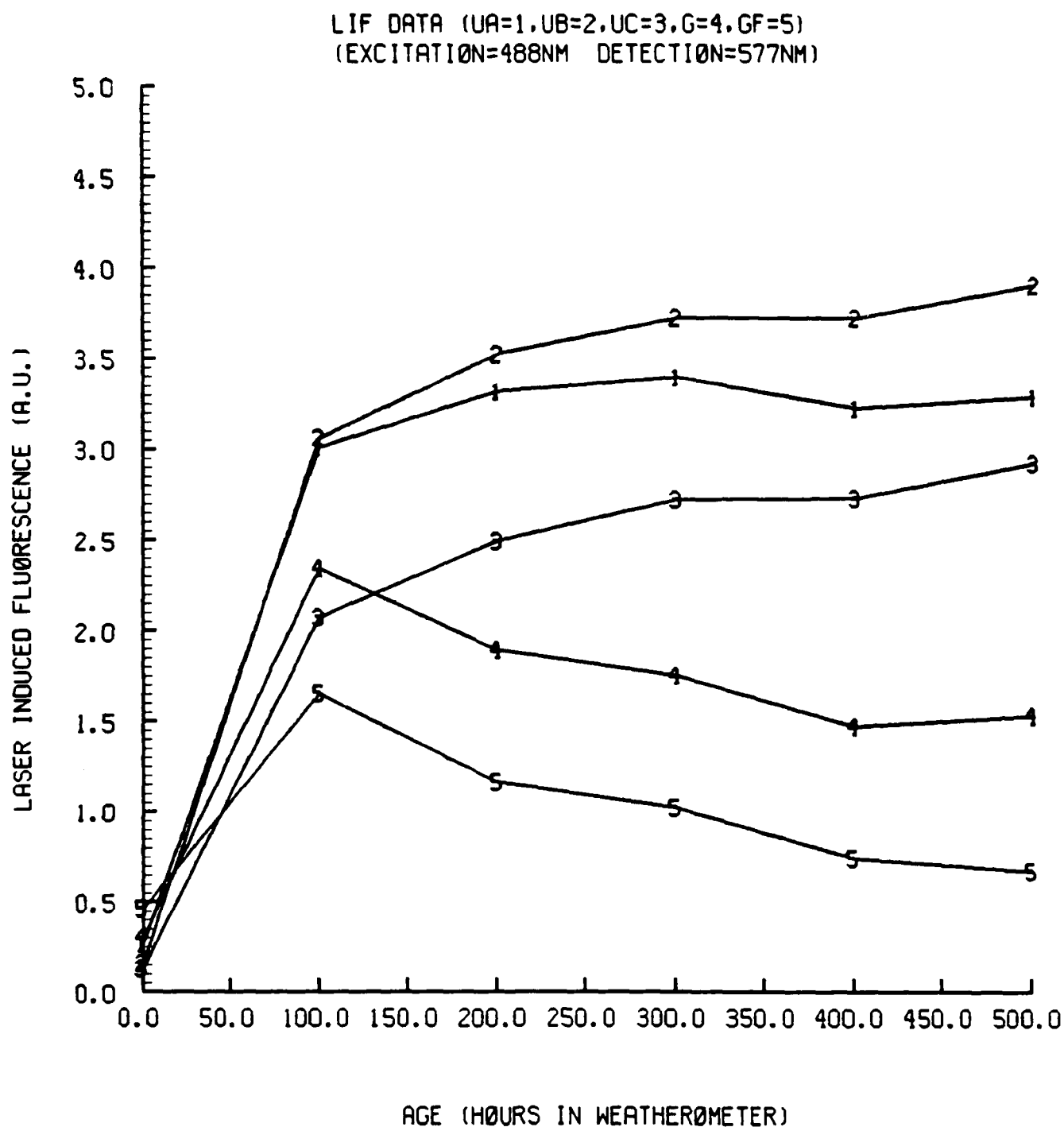


FIGURE 3A. LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE
(Ex: 488 nm; Det: 577 nm; Samples: UA, UB, UC, G, GF; Aging Method:
Weatherometer)

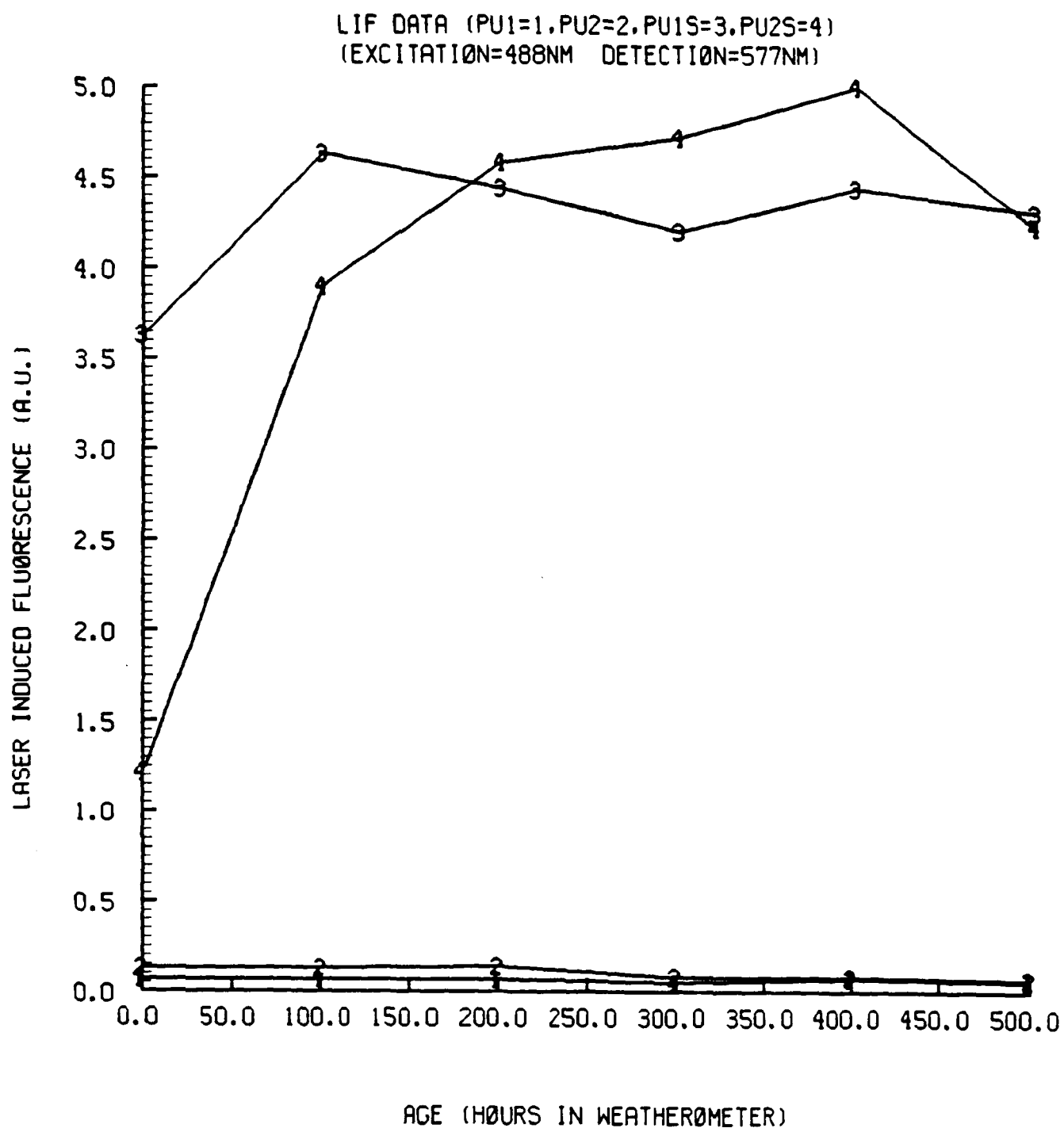


FIGURE 3B. LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE
(Ex: 488 nm; Det: 577 nm; Samples: PU1, PU2, PU1S, PU2S; Aging Method:
Weatherometer)

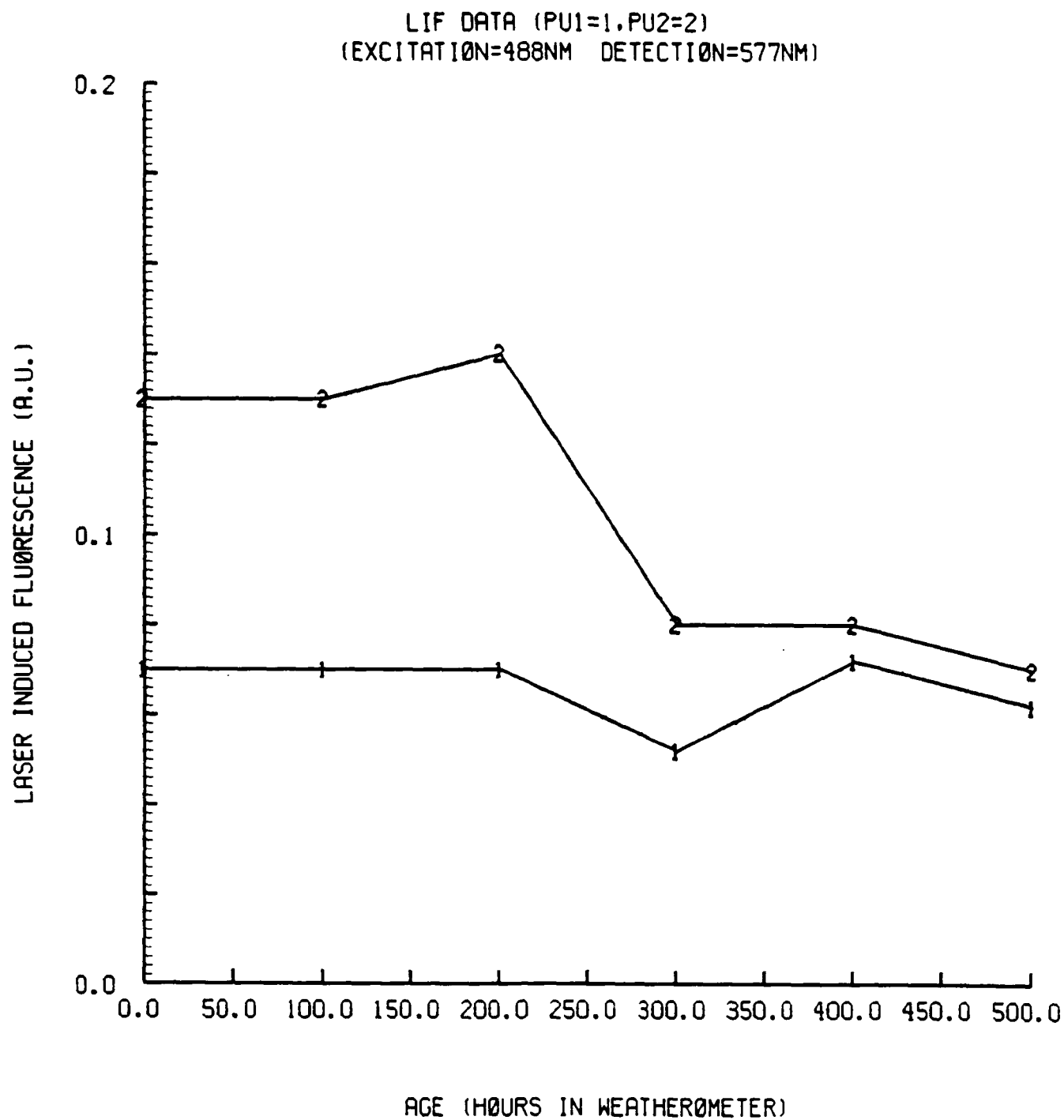


FIGURE 3C. LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE
(Ex: 488 nm; Det: 577 nm; Samples: PU1, PU2; Aging Method: Weatherometer;
Comments: Expanded scale of Figure 3B)

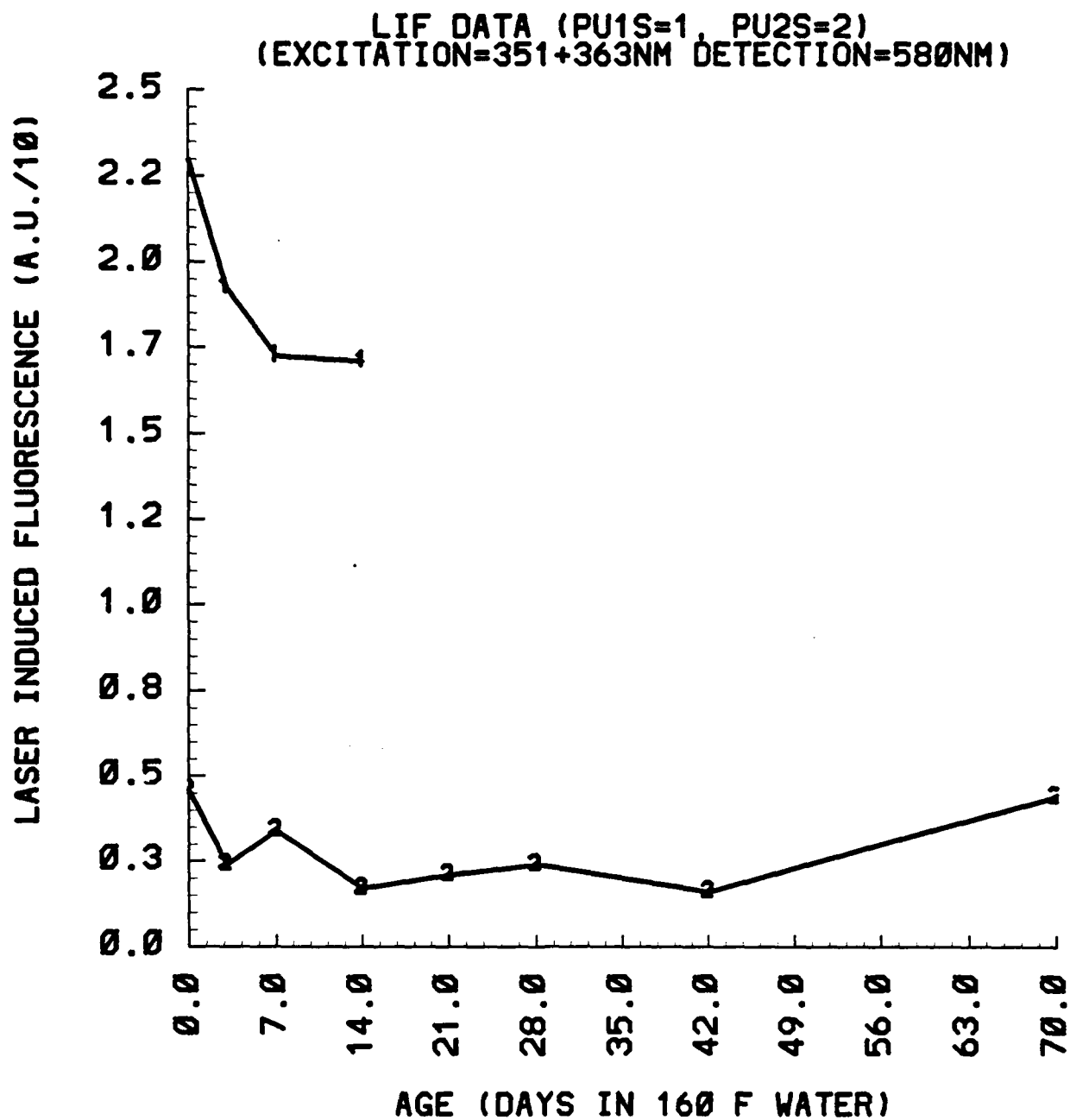


FIGURE 4A. LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE
(Ex: 351+363 nm; Det: 580 nm; Samples: PU1S, PU2S; Aging Method: Hot Water)

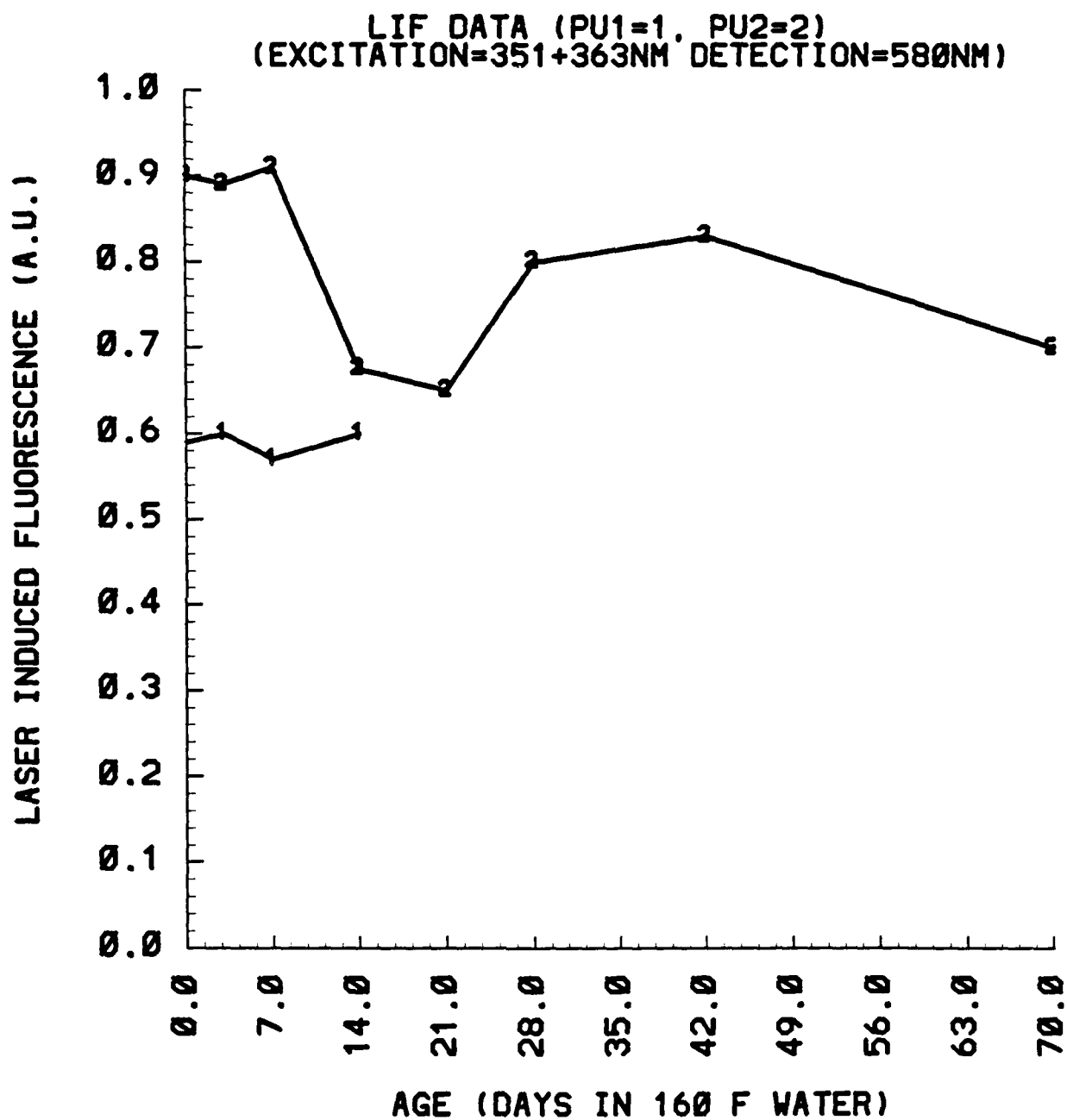


FIGURE 4B. LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF AGE
(Ex: 351+363 nm; Det: 580 nm; Samples: PU1, PU2; Aging Method: Hot Water)

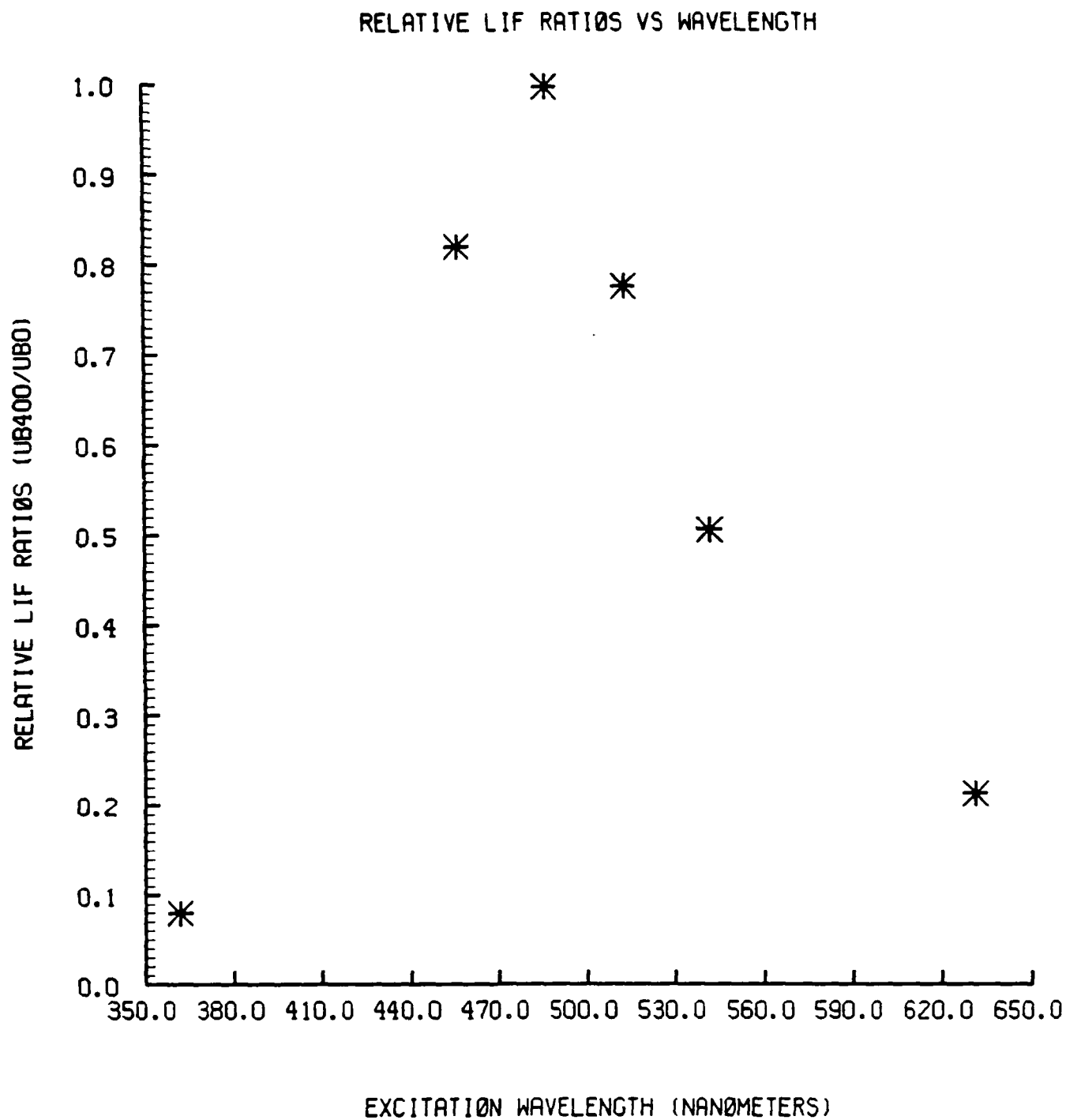


FIGURE 5. RELATIVE LASER-INDUCED-FLUORESCENCE RATIO AS A FUNCTION OF EXCITATION WAVELENGTH (Samples: UB (400 hrs), UB (unaged); Aging Method: Weatherometer)

FLUORESCENCE QUENCHING (UA21DAYS160F)
(488NM/577NM/0.086W/CM2)

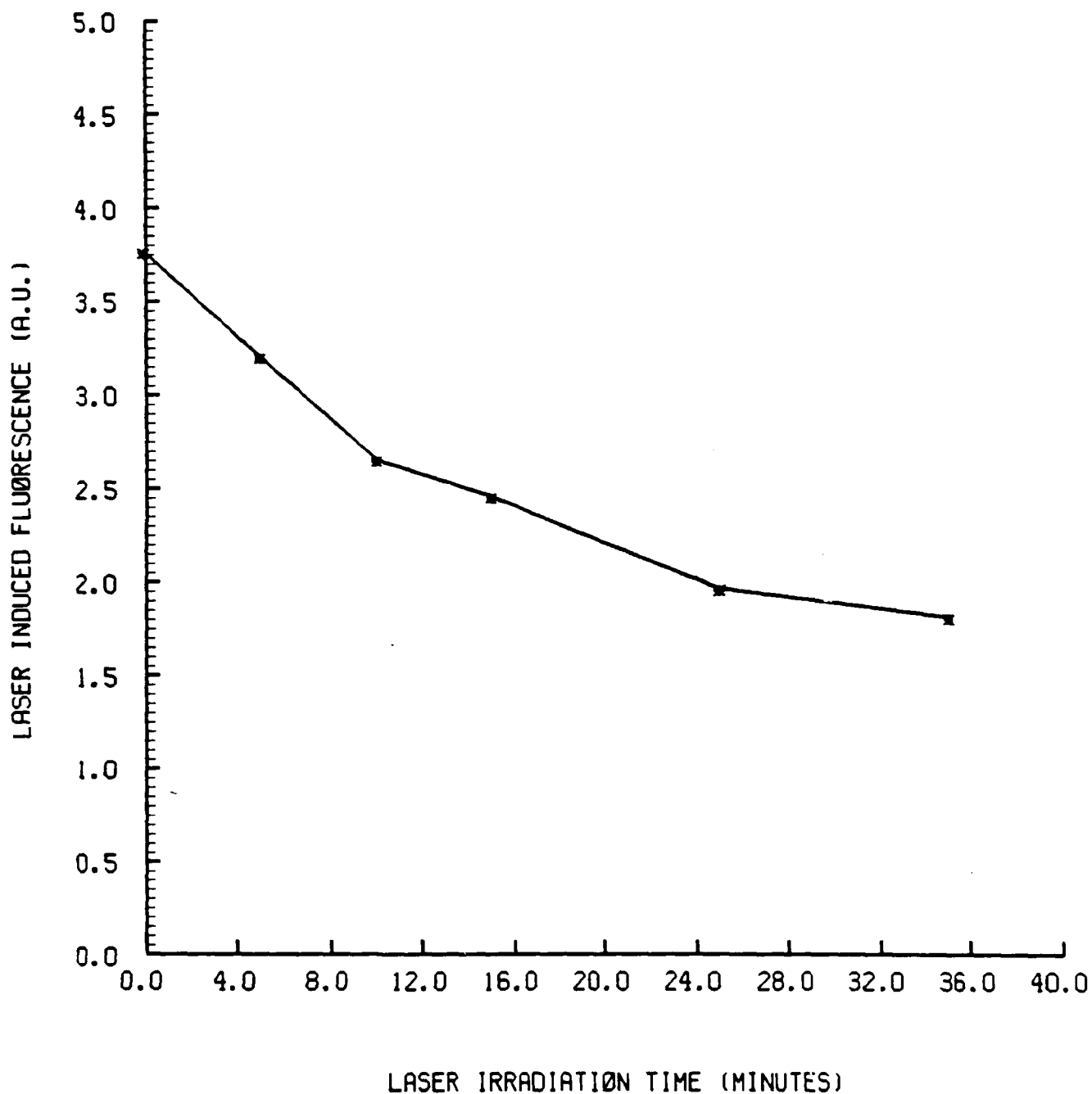


FIGURE 6A. LASER-INDUCED FLUORESCENCE AS A FUNCTION OF LASER IRRADIATION TIME (Ex: 488 nm; Det: 577 nm; Sample: UA (21 days); Aging Method: Hot Water)

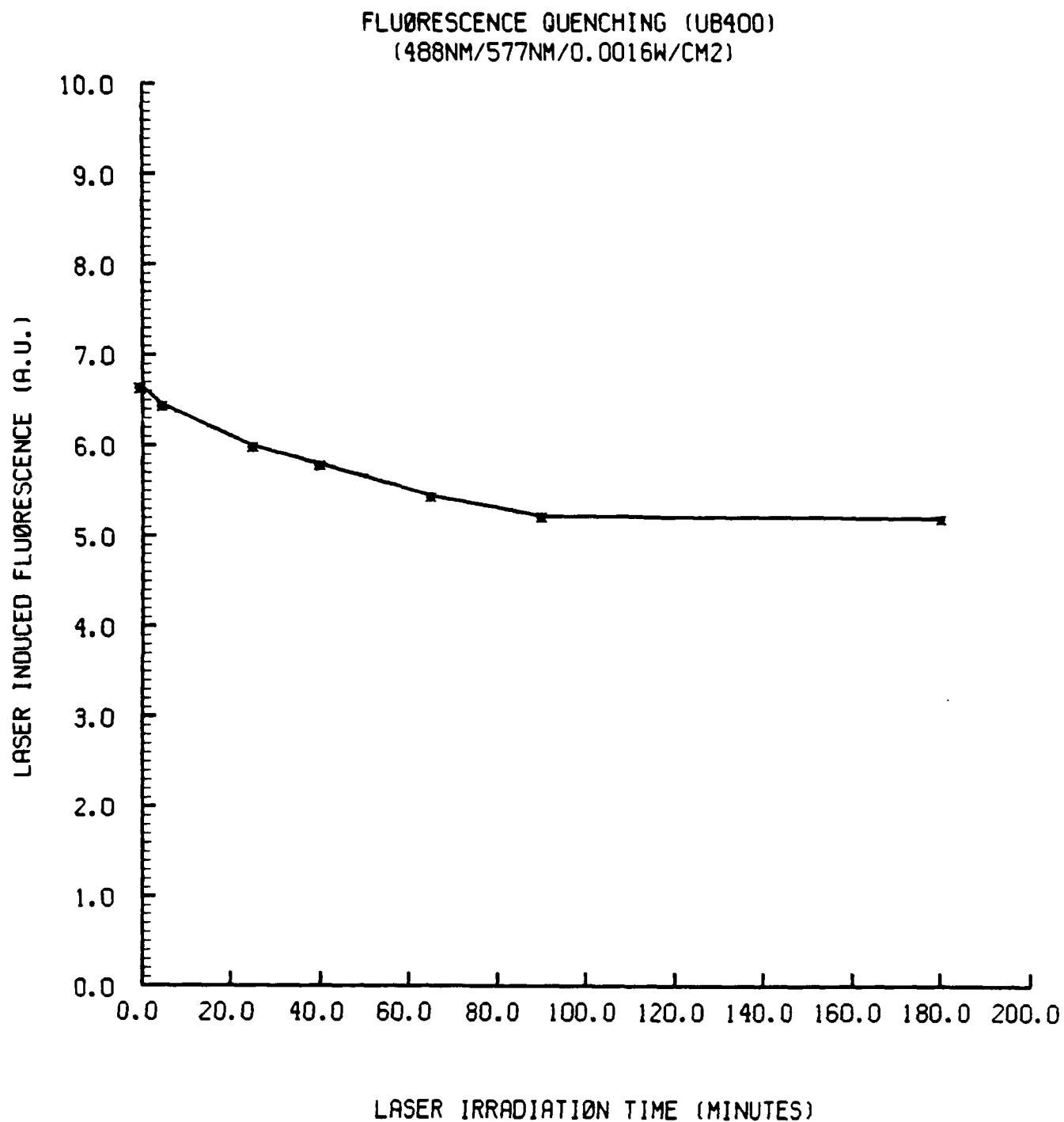


FIGURE 6B. LASER-INDUCED FLUORESCENCE AS A FUNCTION OF LASER IRRADIATION TIME (Ex: 488 nm; Det: 577 nm; Sample: UB (400 hrs); Aging Method: Weatherometer; Comments: Laser power density was less than for Figure 6A)

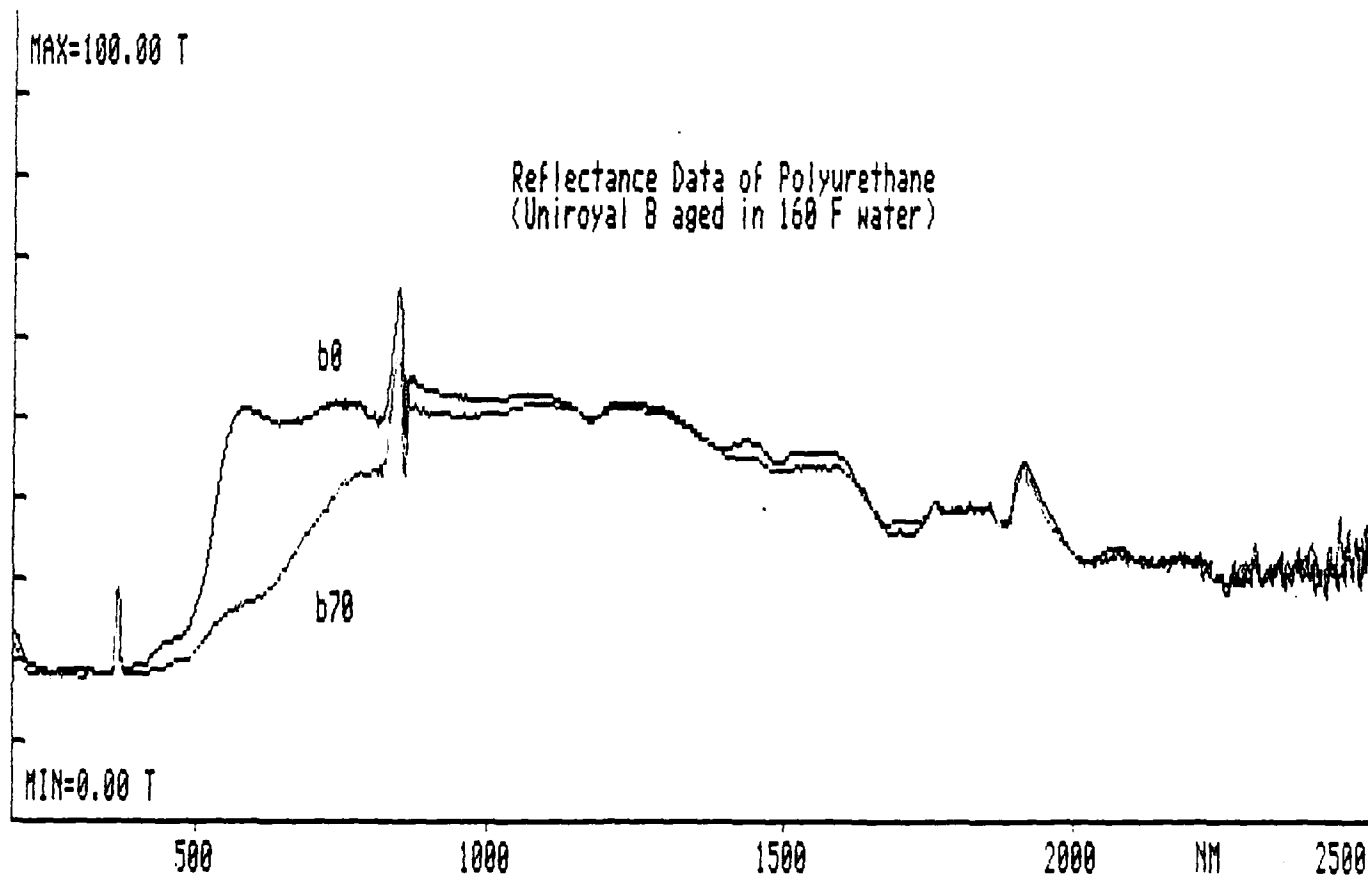


FIGURE 7A. REFLECTANCE AS A FUNCTION OF WAVELENGTH (Samples: UB (unaged) and UB (70 days); Aging Method: Hot Water; Comments: Anomalies at approximately 360 nm and 860 nm are instrumental artifacts)

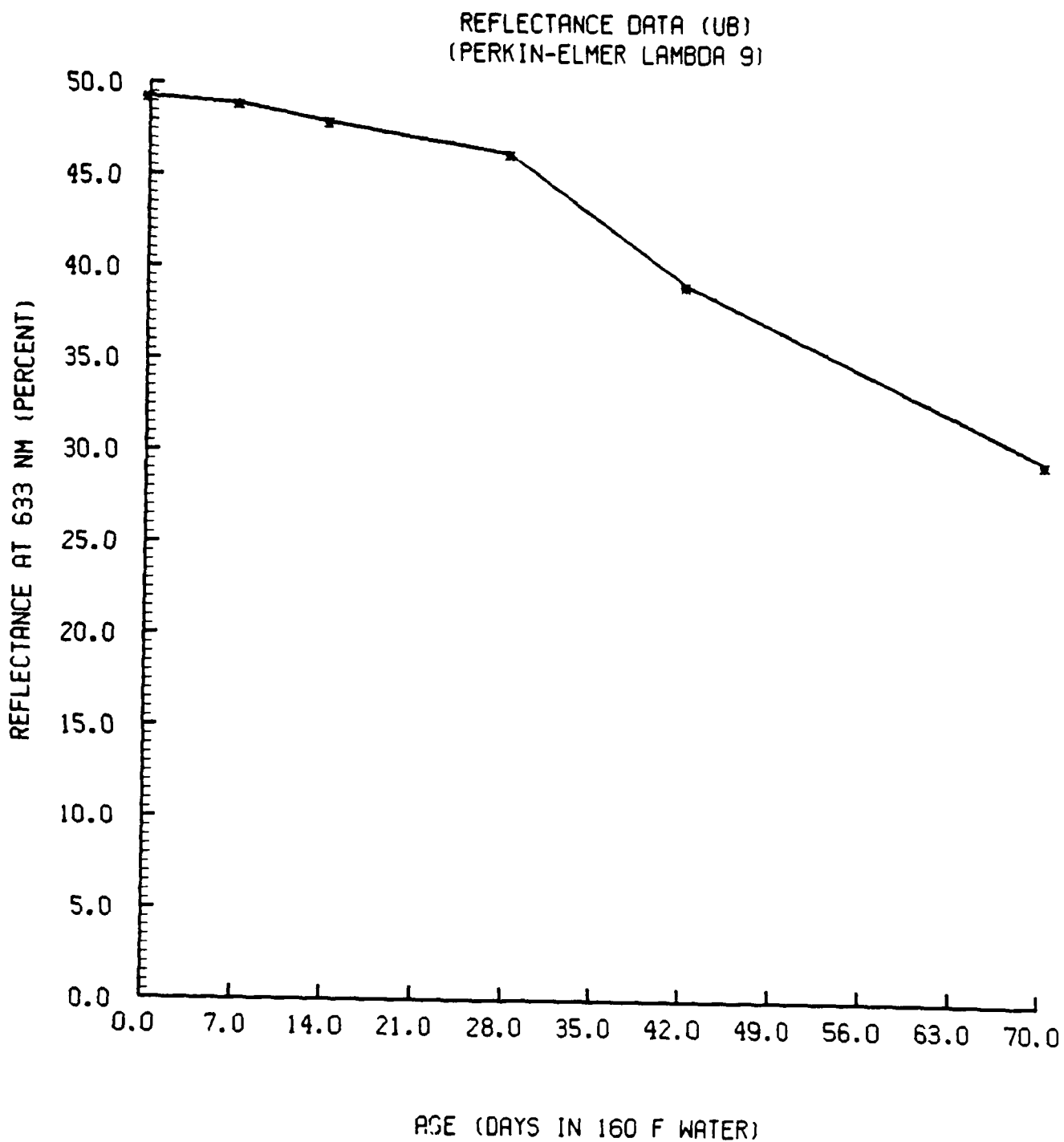


FIGURE 7B. REFLECTANCE AT 633 NM AS A FUNCTION OF AGE (Ex: 633 nm; Det: 633 nm; Samples: UB; Aging Method: Hot Water)

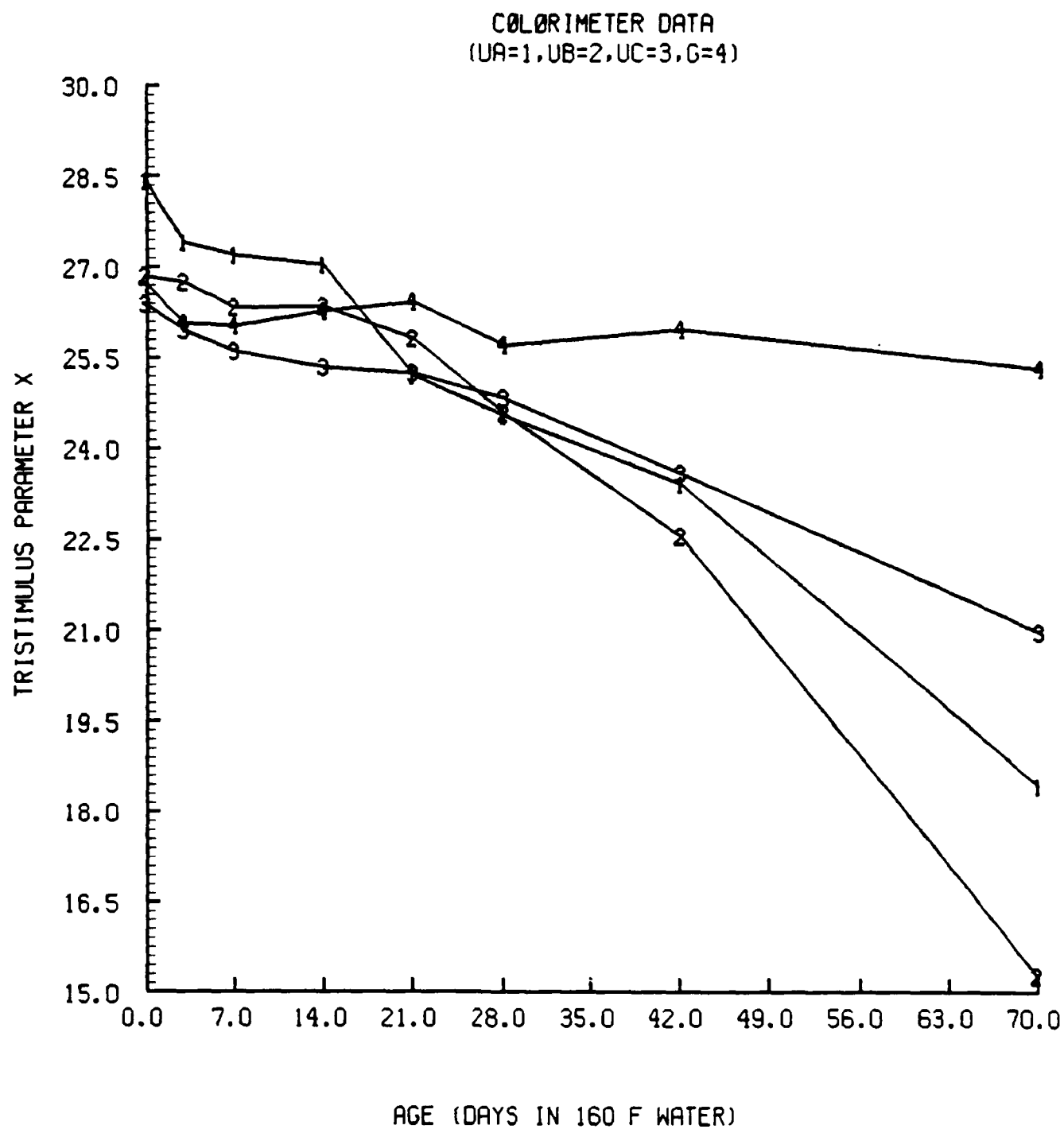


FIGURE 7C. "X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: UA, UB, UC, G; Aging Method: Hot Water)

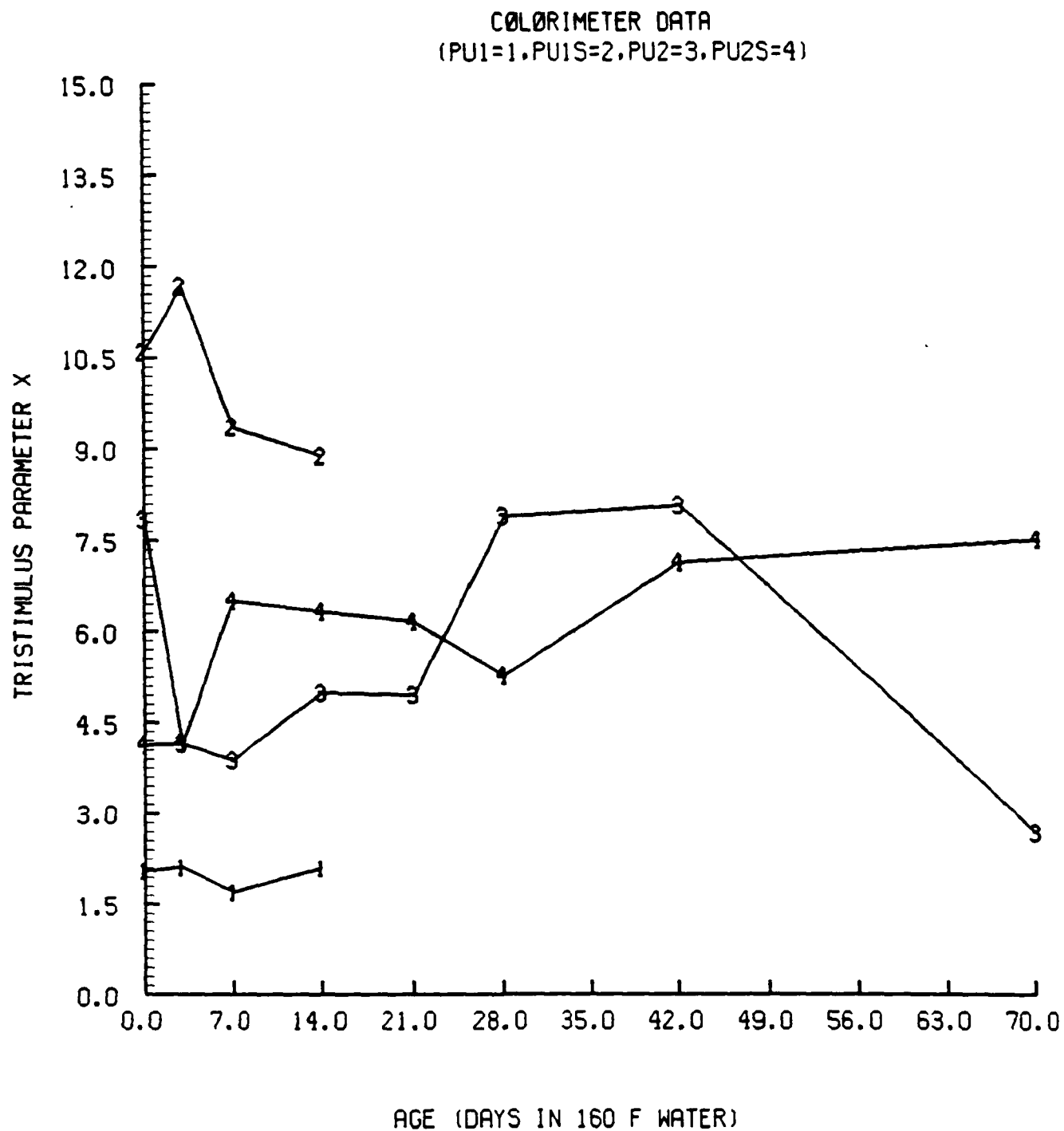


FIGURE 7D. "X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: PU1, PU1S, PU2, PU2S; Aging Method: Hot Water)

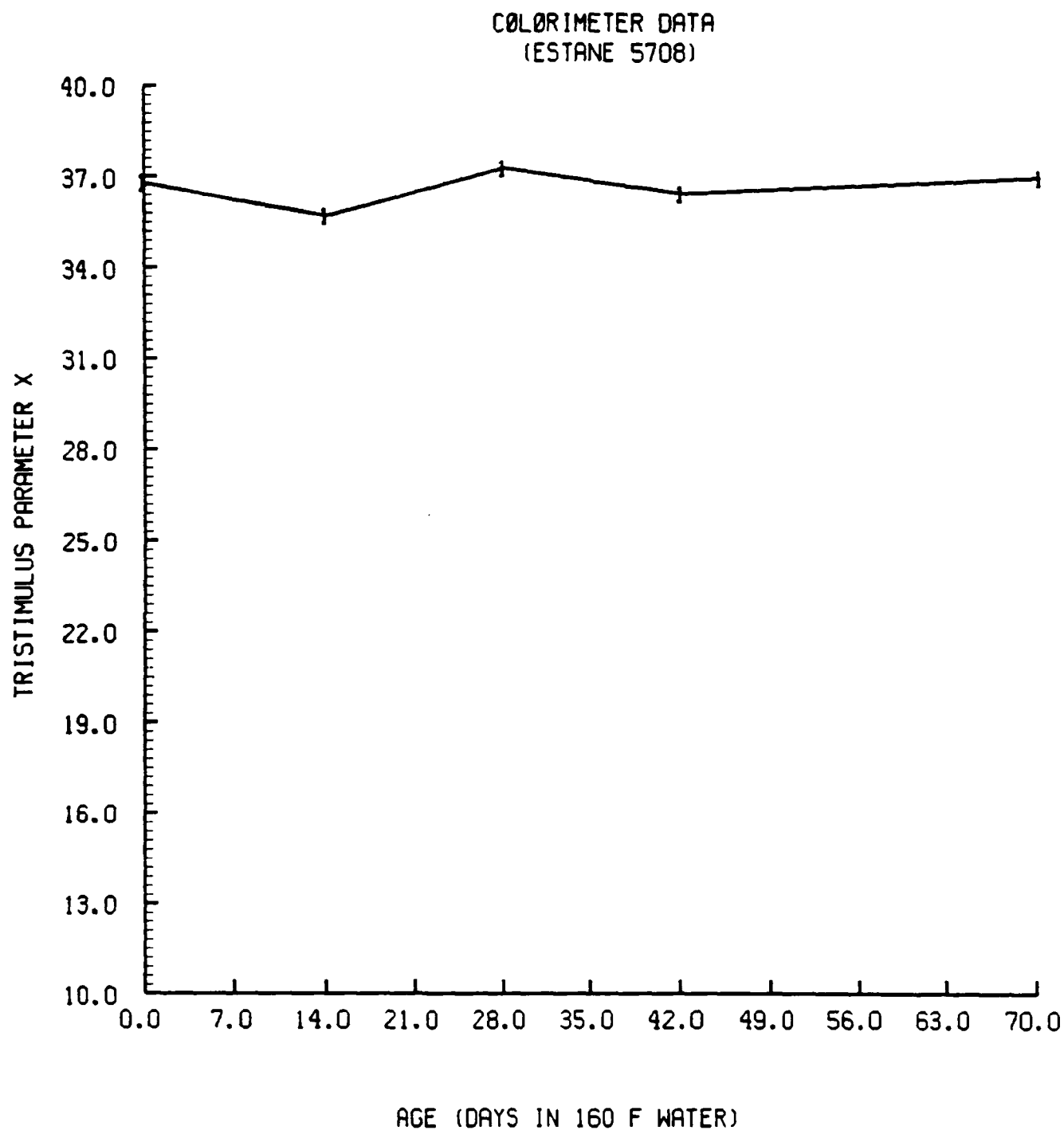


FIGURE 7E. "X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: EST; Aging Method: Hot Water);

COLORIMETER DATA
(LU-2 SEMITRANSSPARENT)

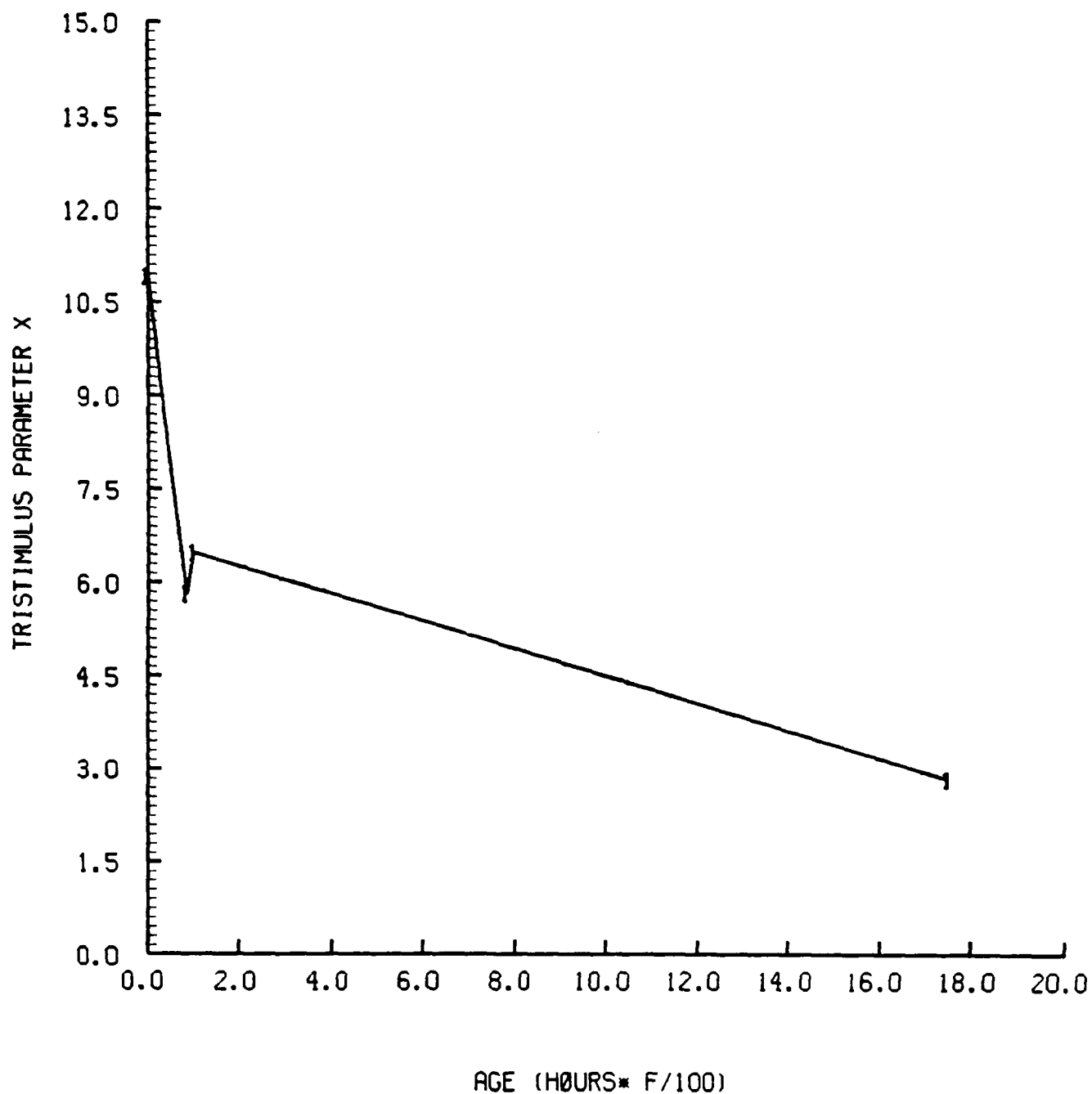


FIGURE 7F. "X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: LU2; Aging Method: Hot Water; Comments: Note that age coordinate slightly differs from other graphs)

COLORIMETER DATA
(UA=1, UB=2, UC=3, G=4)

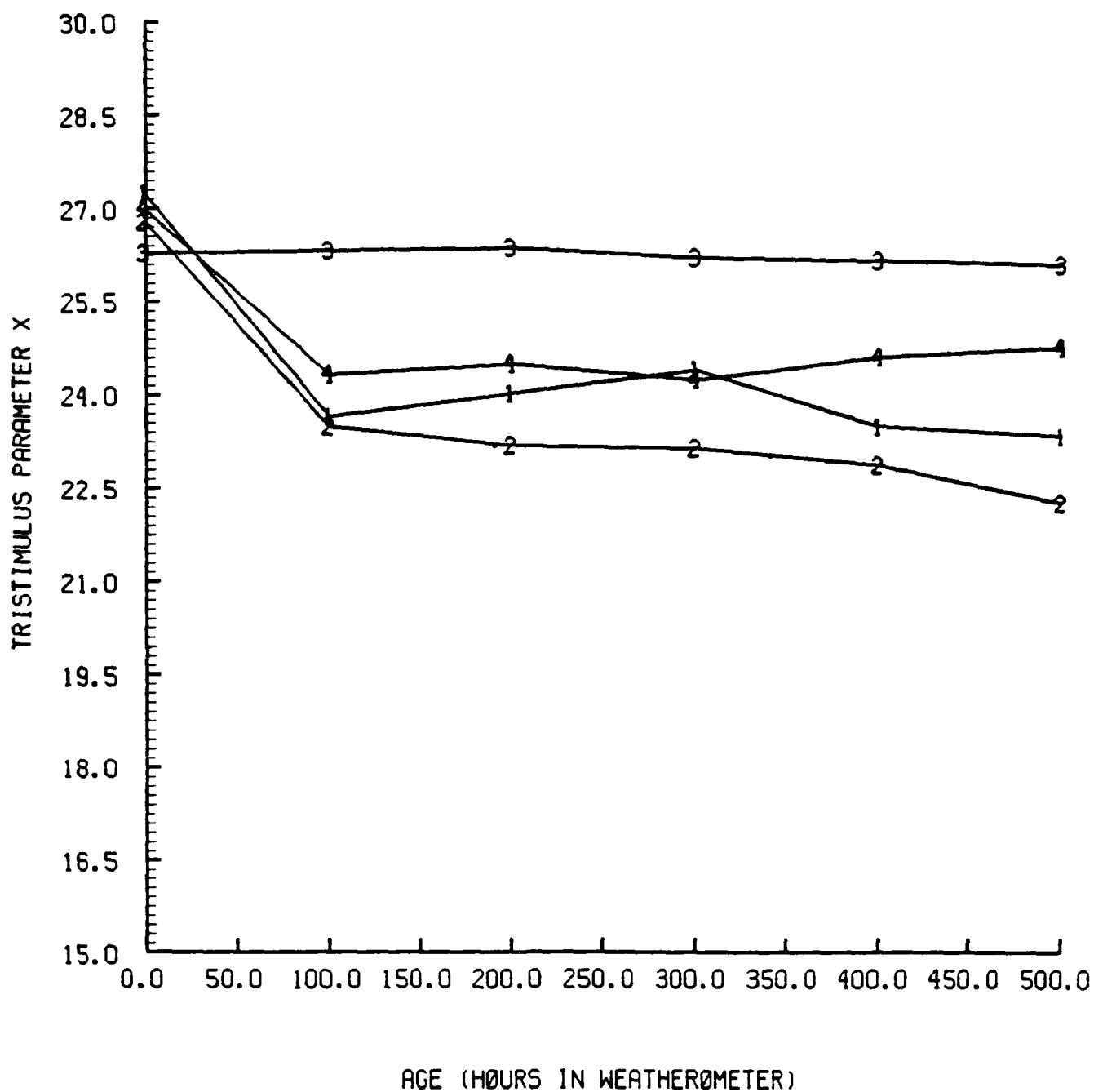


FIGURE 7G. "X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: UA, UB, UC, G; Aging Method: Weatherometer)

COLORIMETER DATA
(PU1=1, PU1S=2, PU2=3, PU2S=4)

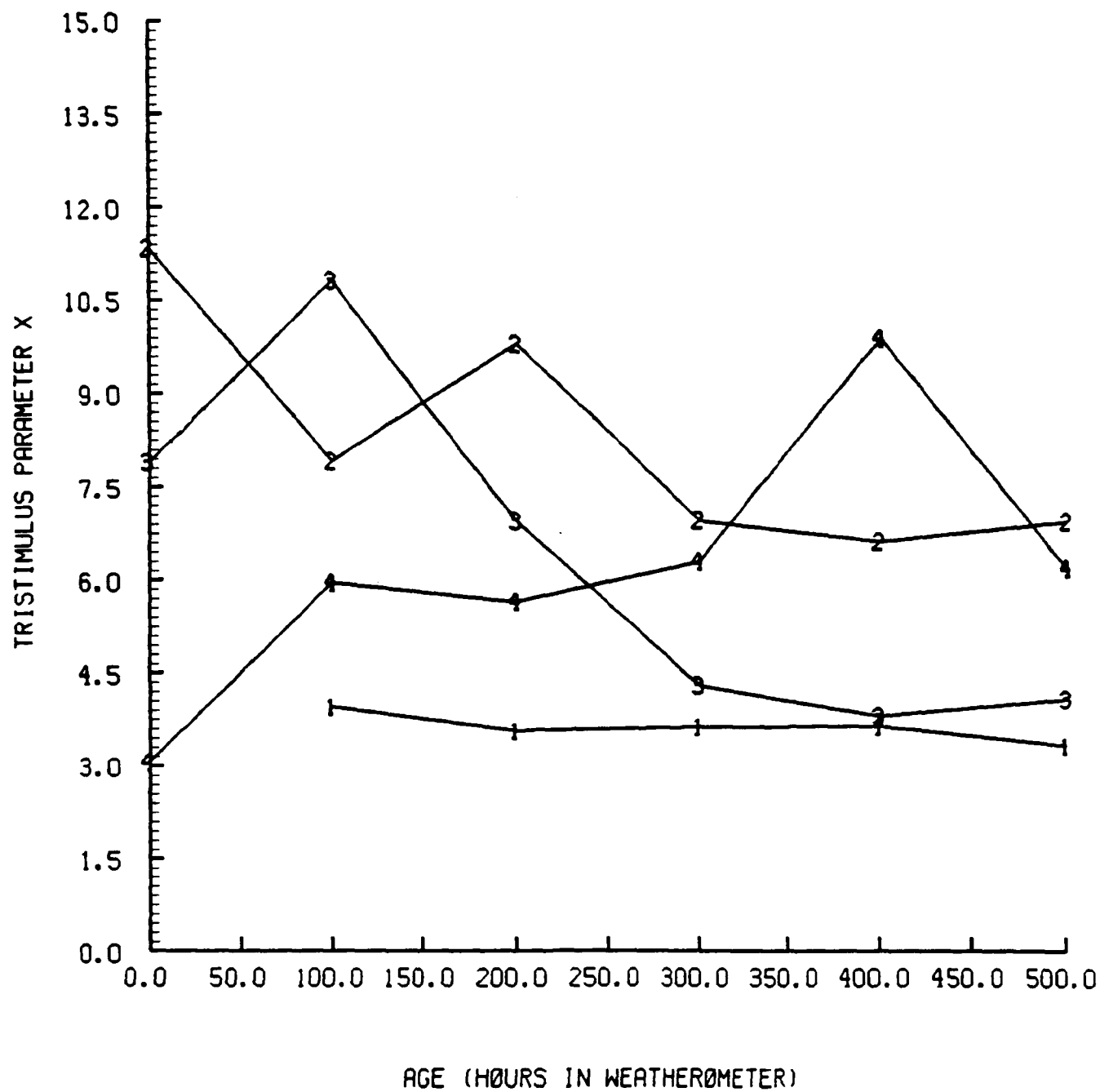


FIGURE 7H. "X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: PU1, PU1S, PU2, PU2S; Aging Method: Weatherometer)

COLORIMETER DATA GOODYEAR FABRIC

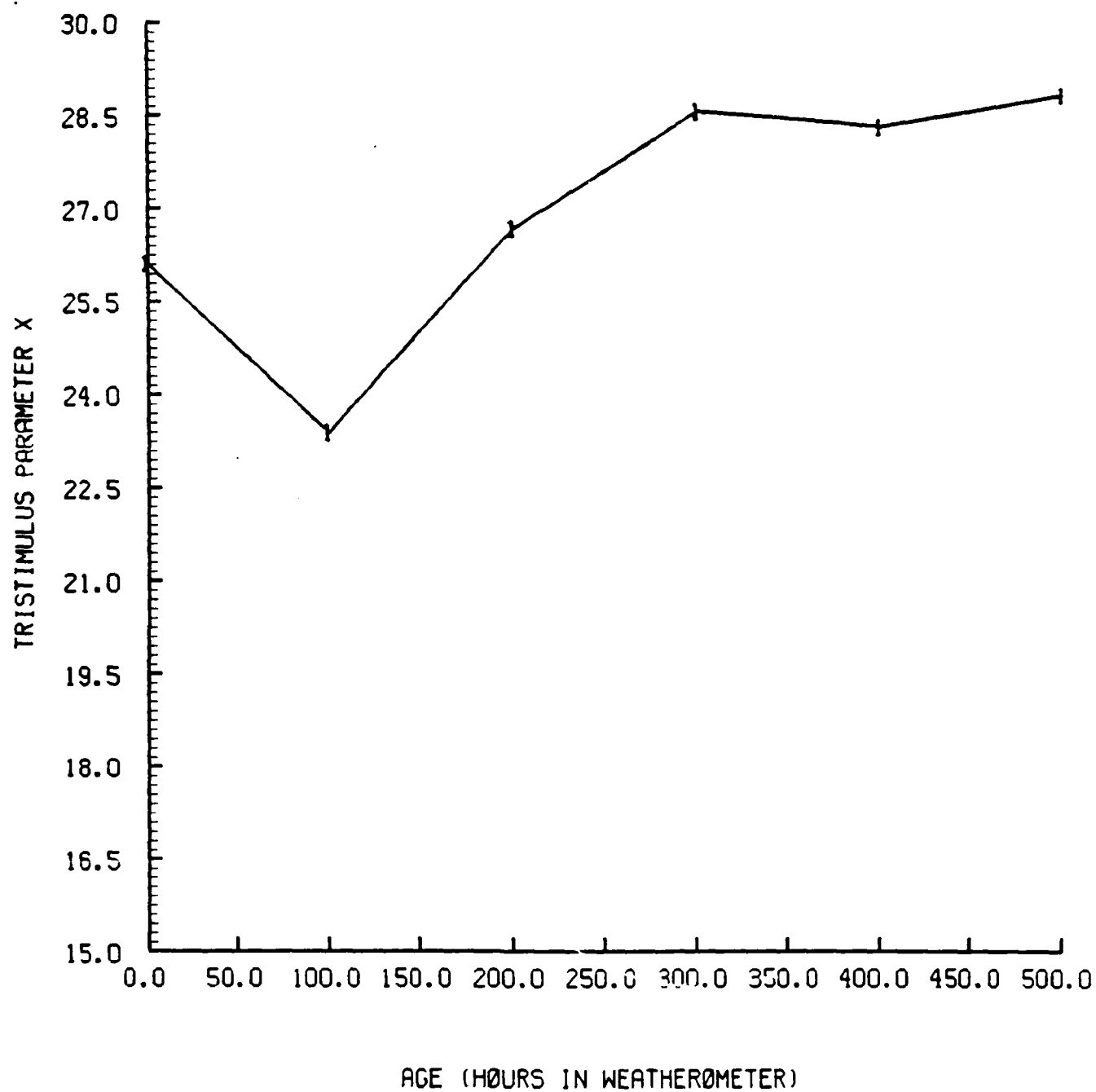


FIGURE 7I. "X" TRISTIMULUS PARAMETER AS A FUNCTION OF AGE (Samples: GF; Aging Method: Weatherometer);

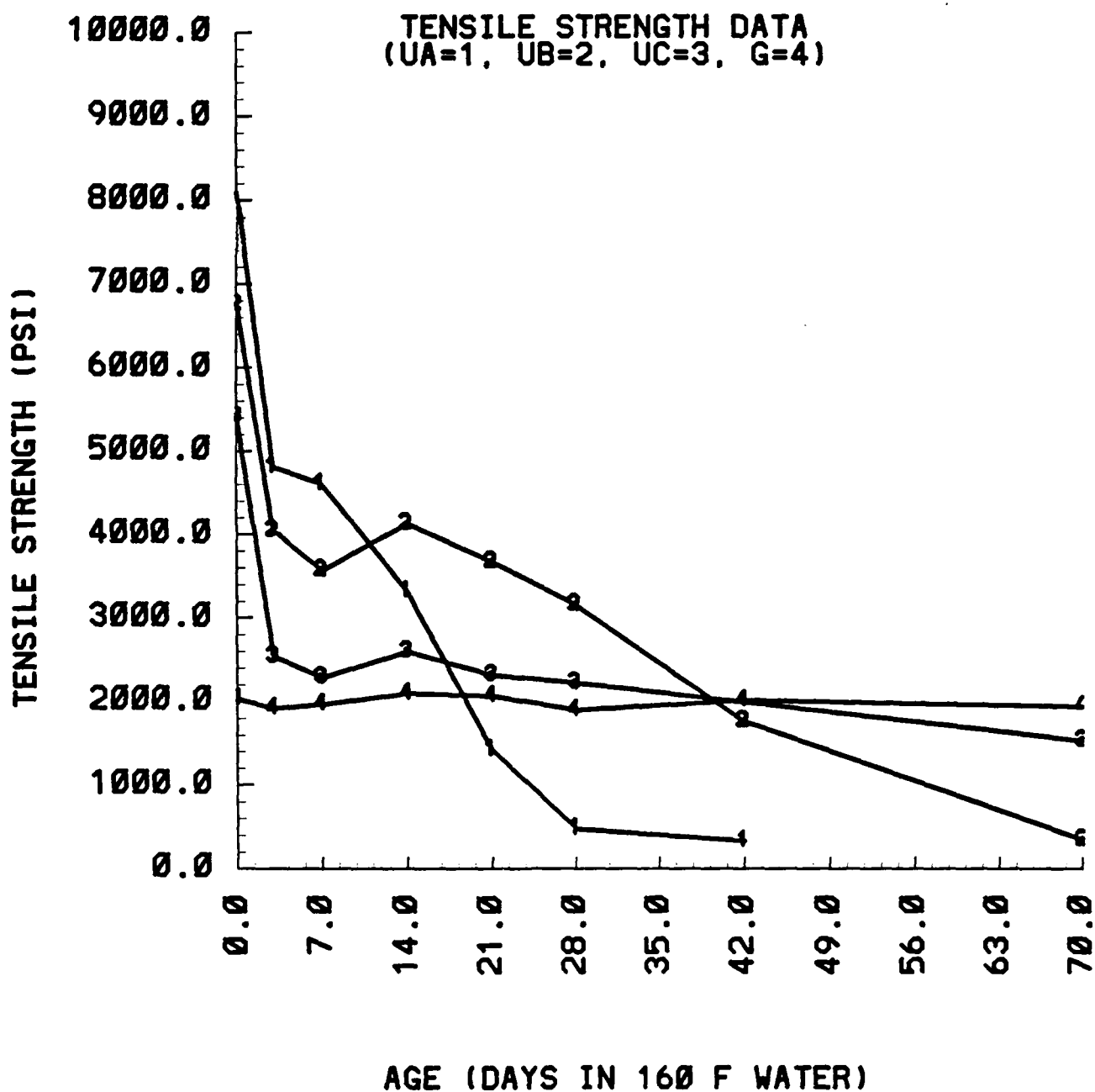


FIGURE 8A. TENSILE STRENGTH AS A FUNCTION OF AGE (Samples: UA, UB, UC, G; Aging Method: Hot Water; Comments: Data courtesy of U.S. Army Belvoir R,D,&E Center)

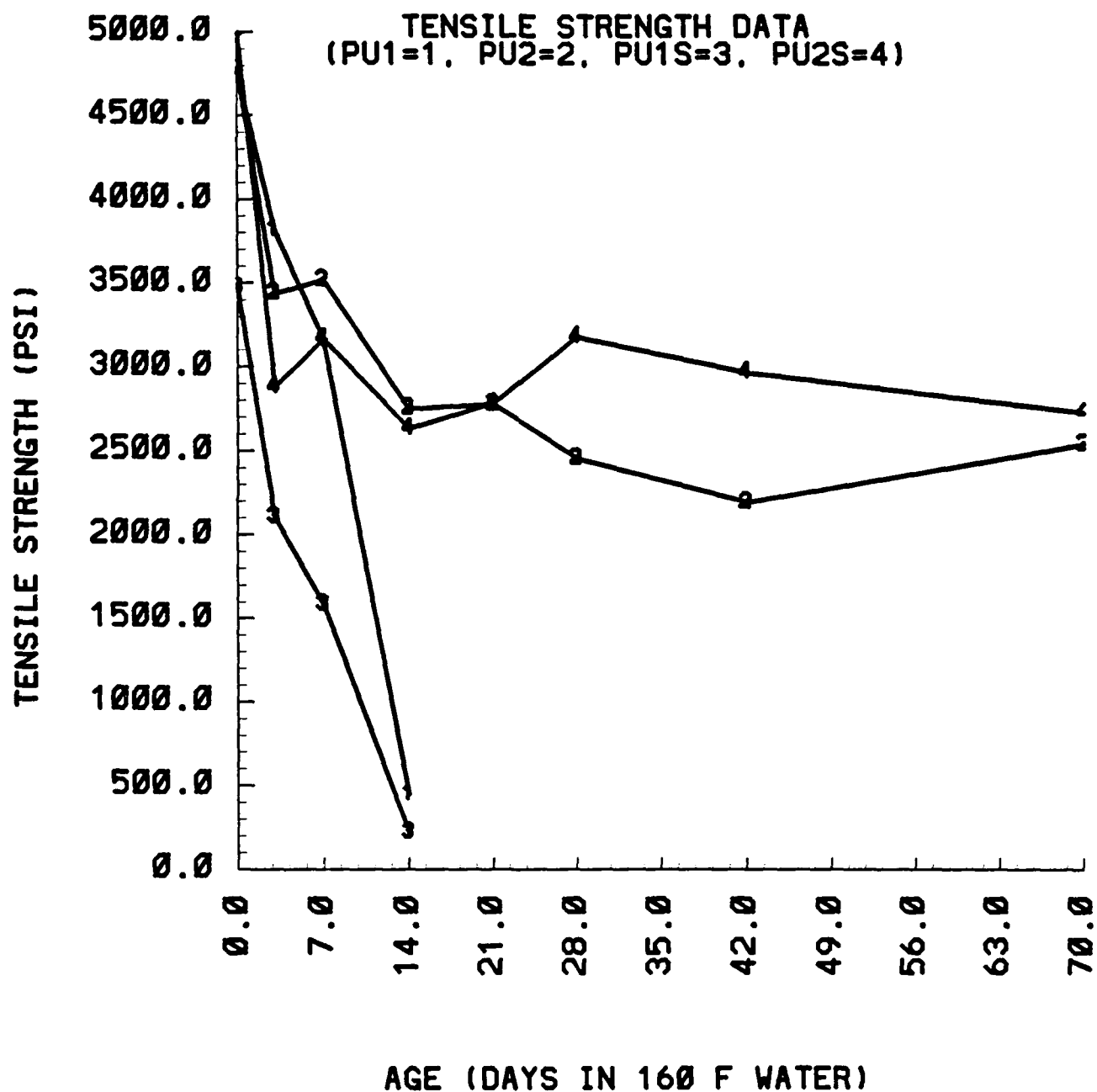


FIGURE 8B. TENSILE STRENGTH AS A FUNCTION OF AGE (Samples: PU1, PU2, PU1S, PU2S; Aging Method: Hot Water; Comments: Data courtesy of U.S. Army Belvoir R,D,&E Center)

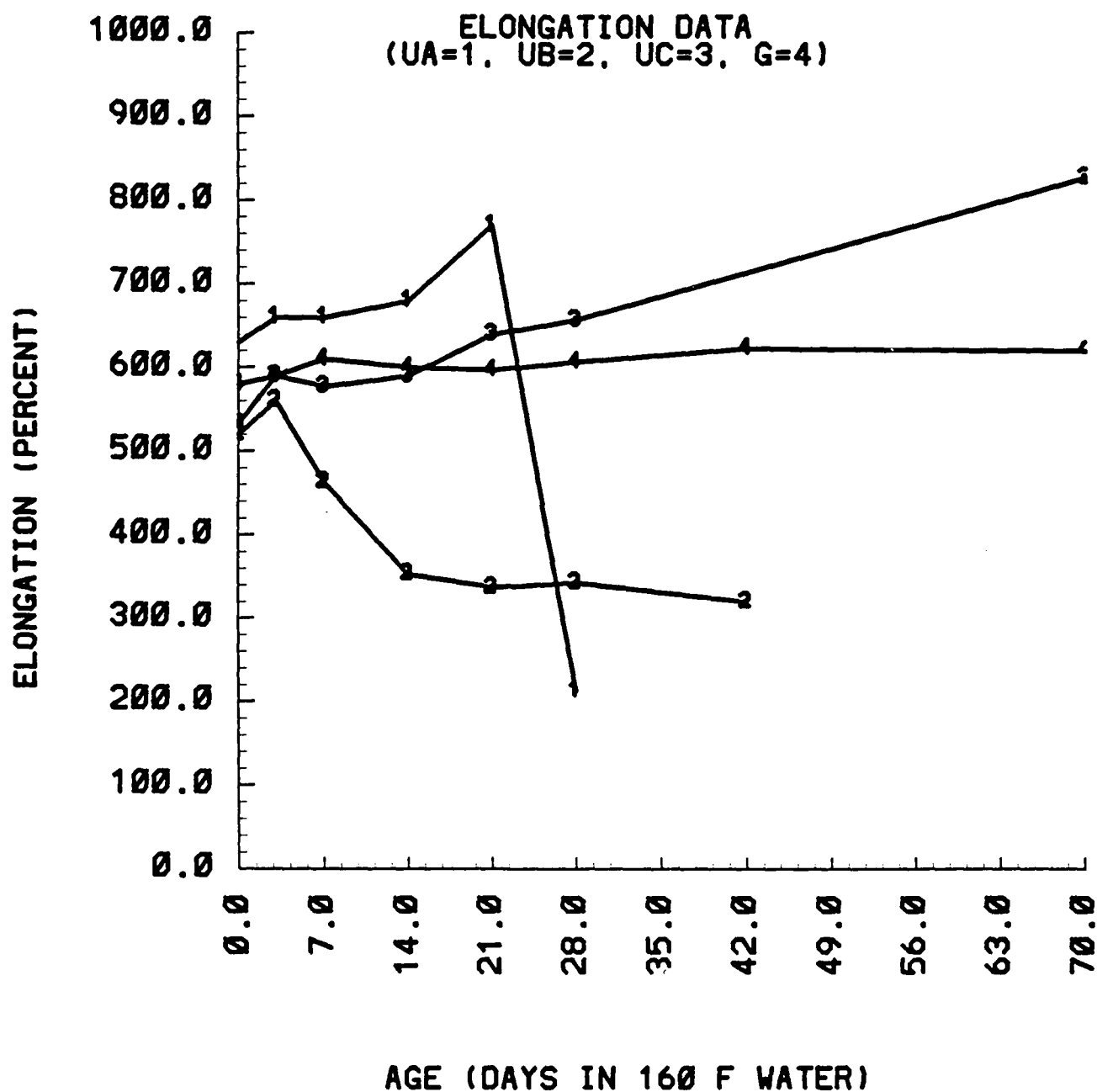


FIGURE 9A. ELONGATION AS A FUNCTION OF AGE (Samples: UA, UB, UC, G; Aging Method: Hot Water; Comments: Data courtesy of U.S. Army Belvoir R,D,&E Center)

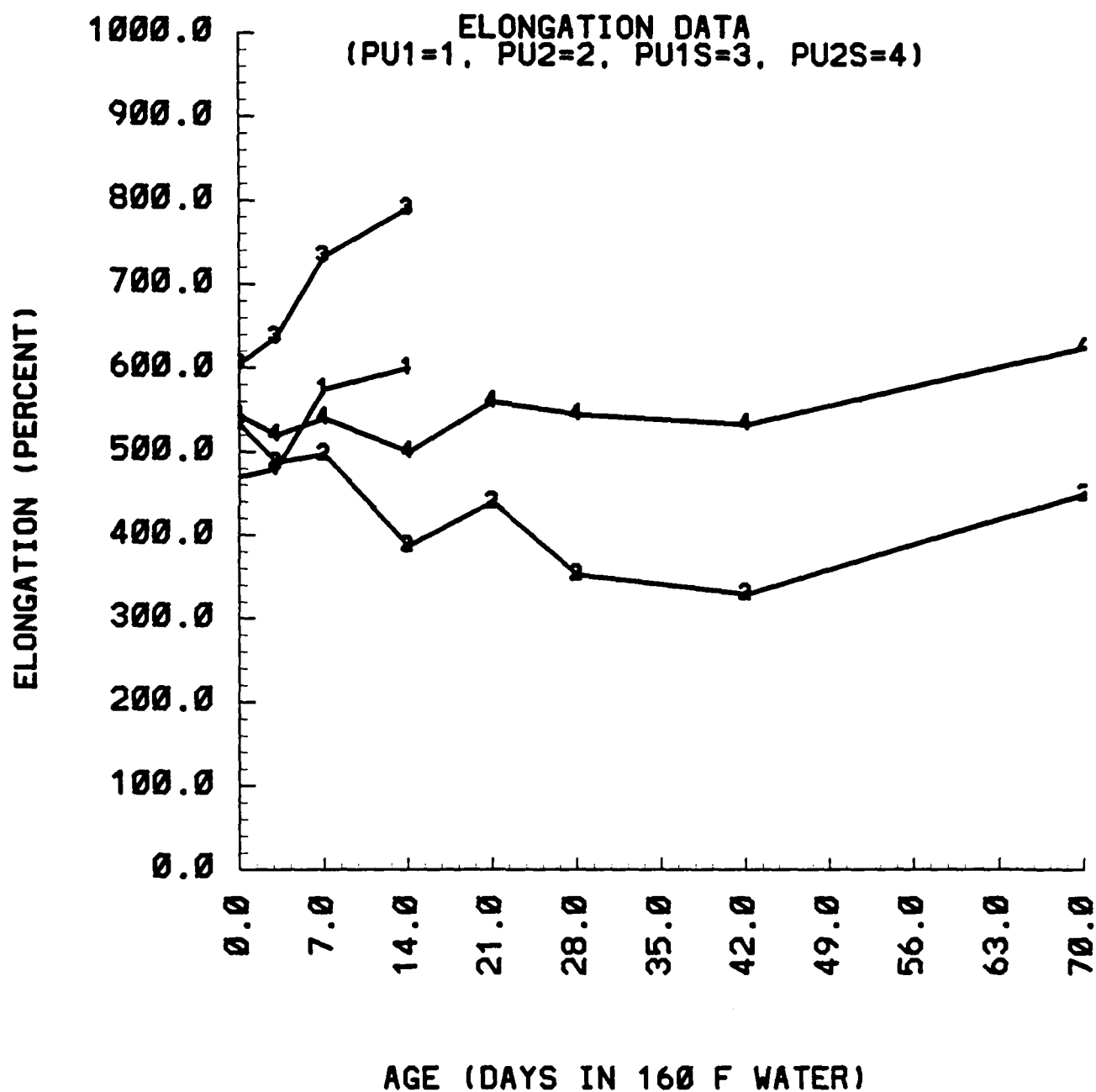


FIGURE 9B. ELONGATION AS A FUNCTION OF AGE (Samples: PU1, PU2, PU1S, PU2S; Aging Method: Hot Water; Comments: Data courtesy of U.S. Army Belvoir R,D,&E Center)

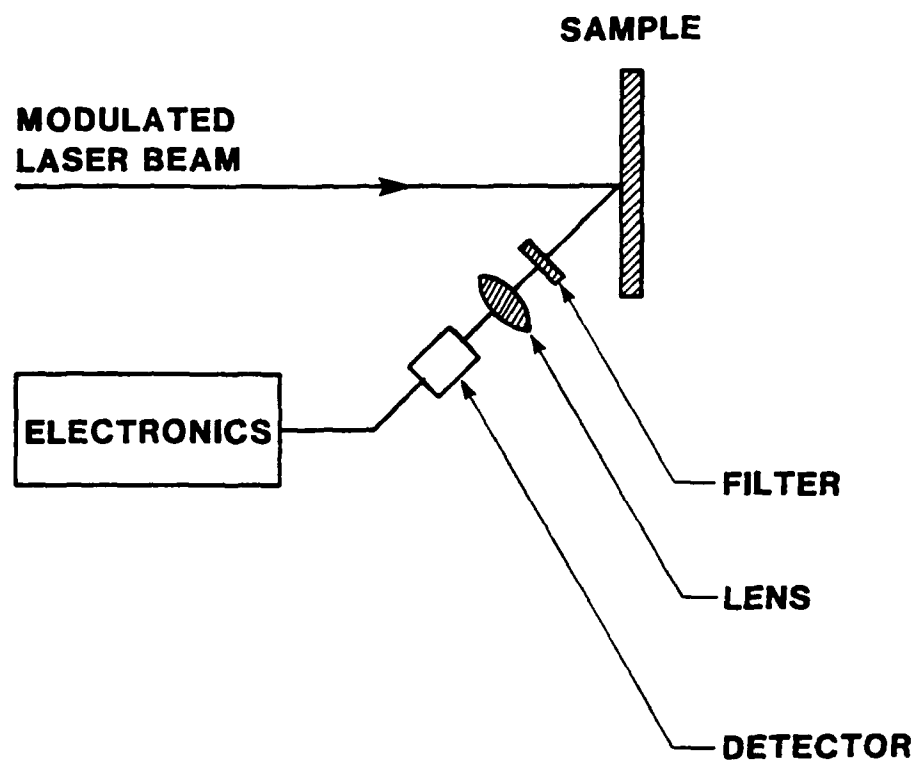


FIGURE 10. EXPERIMENTAL APPARATUS FOR MEASURING INTEGRATED FLUORESCENCE

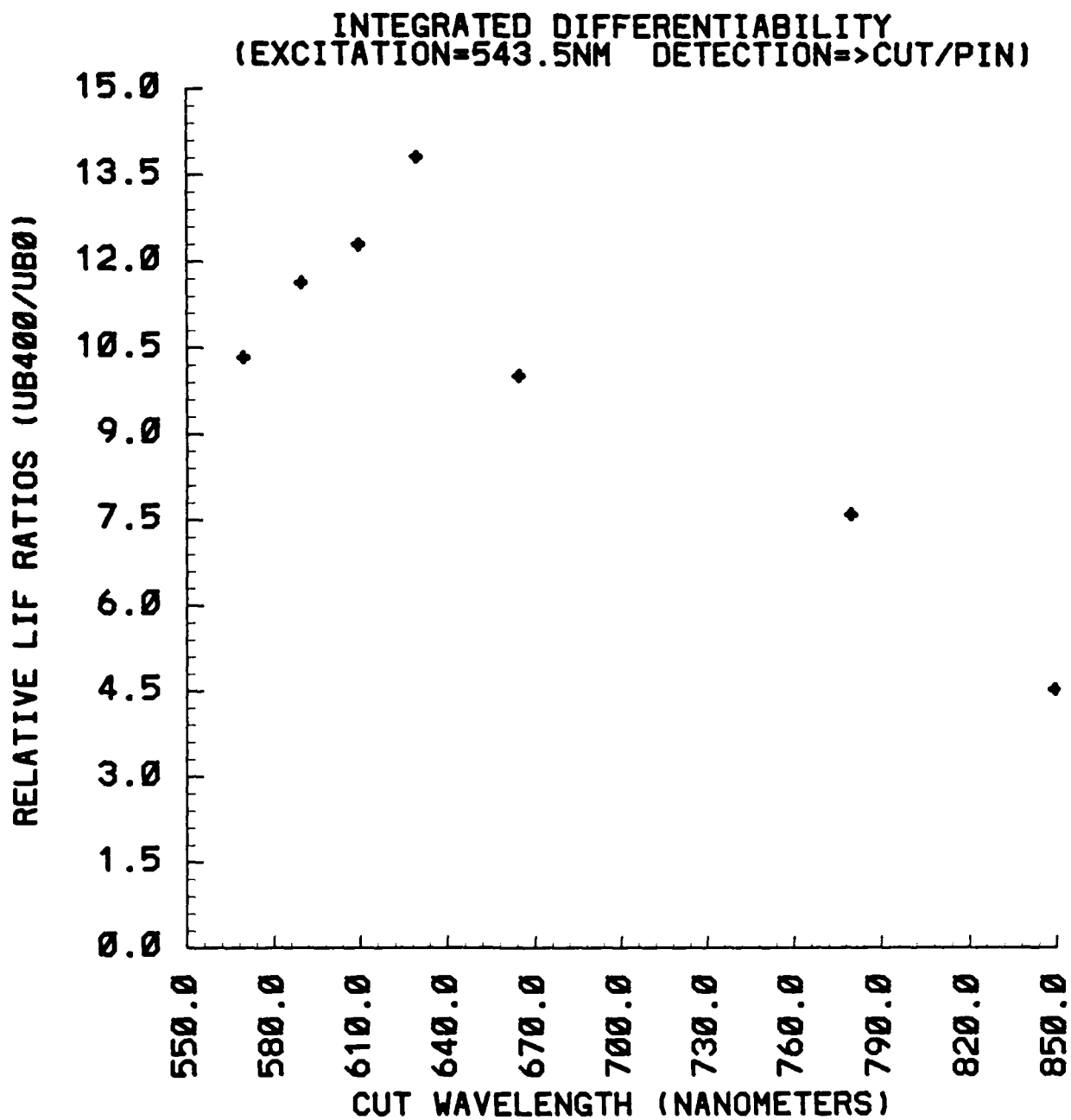


FIGURE 11A. INTEGRATED DIFFERENTIABILITY (Ex: 543.5 nm; Samples: UB; Aging Method: Weatherometer)

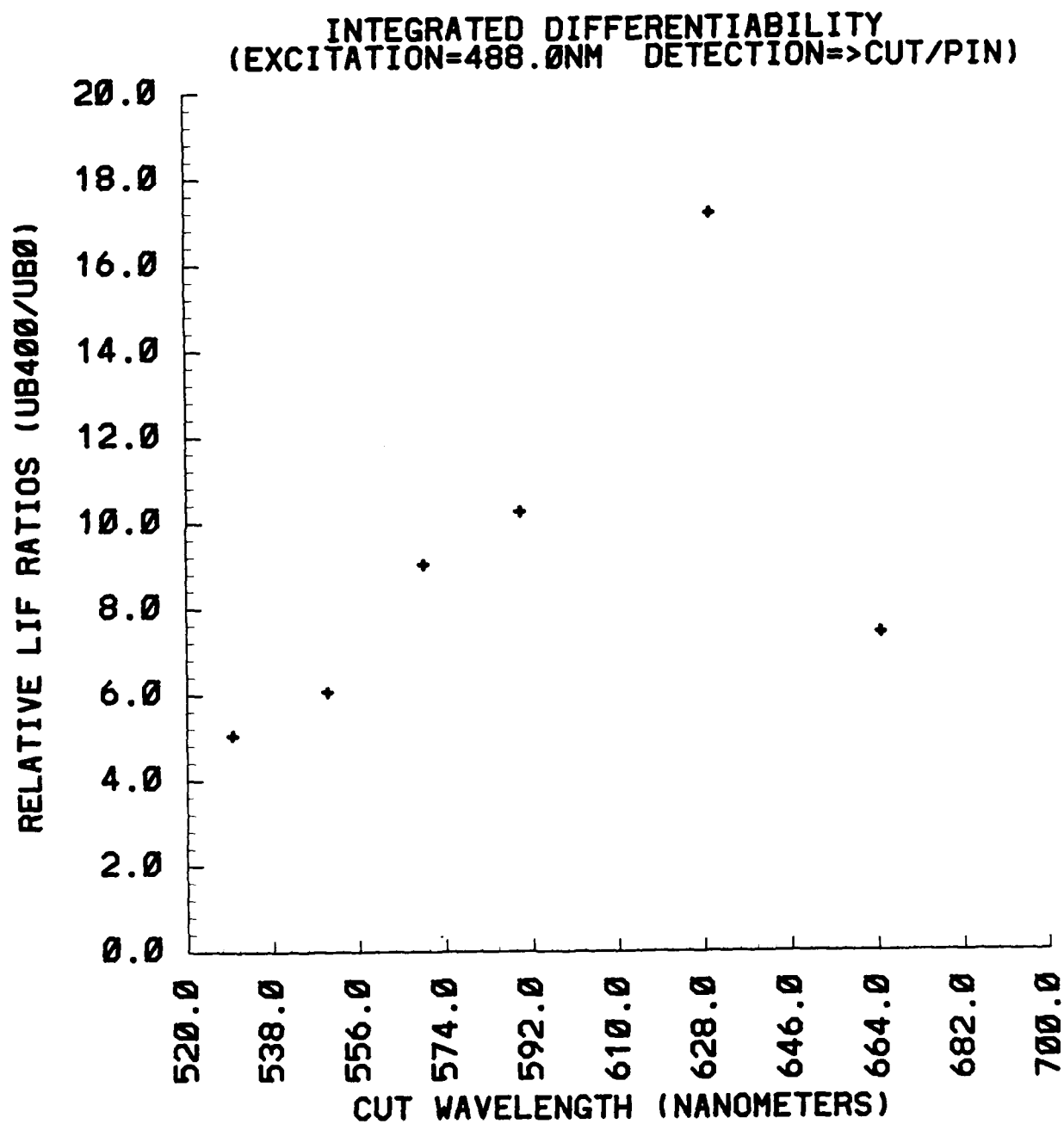


FIGURE 11B. INTEGRATED DIFFERENTIABILITY (Ex: 488 nm; Samples: UB;
Aging Method: Weatherometer)

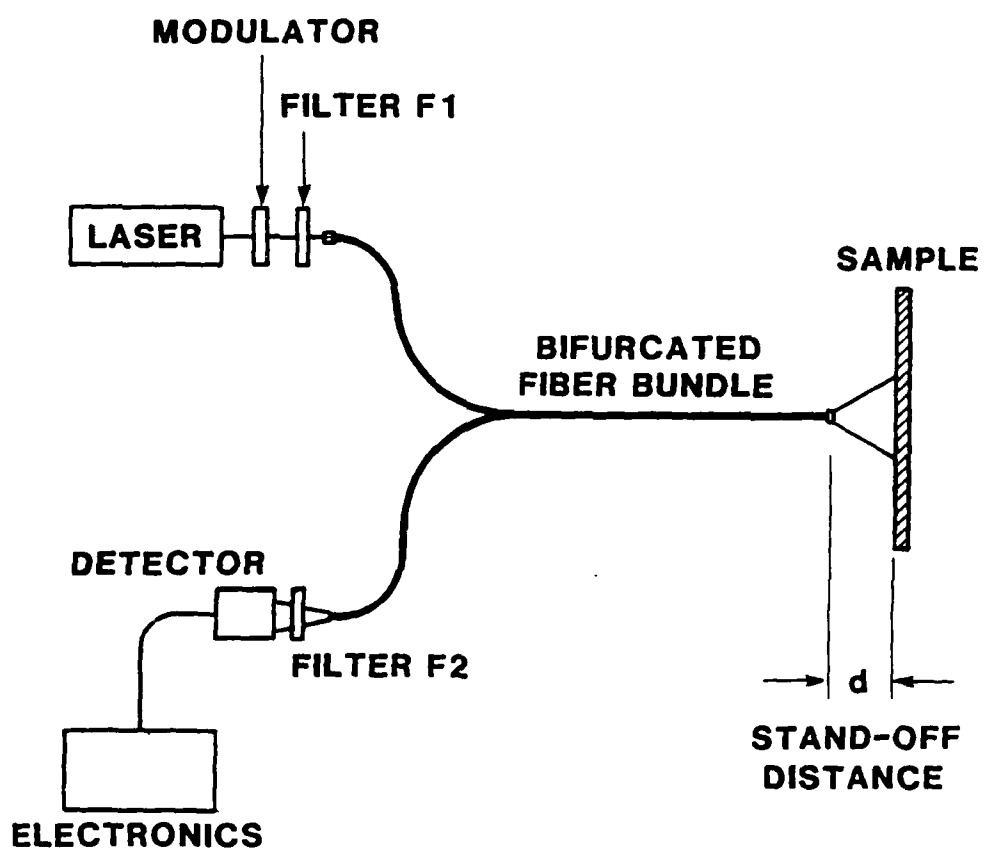


FIGURE 12. EXPERIMENTAL APPARATUS USING A BIFURCATED FIBER-OPTIC BUNDLE

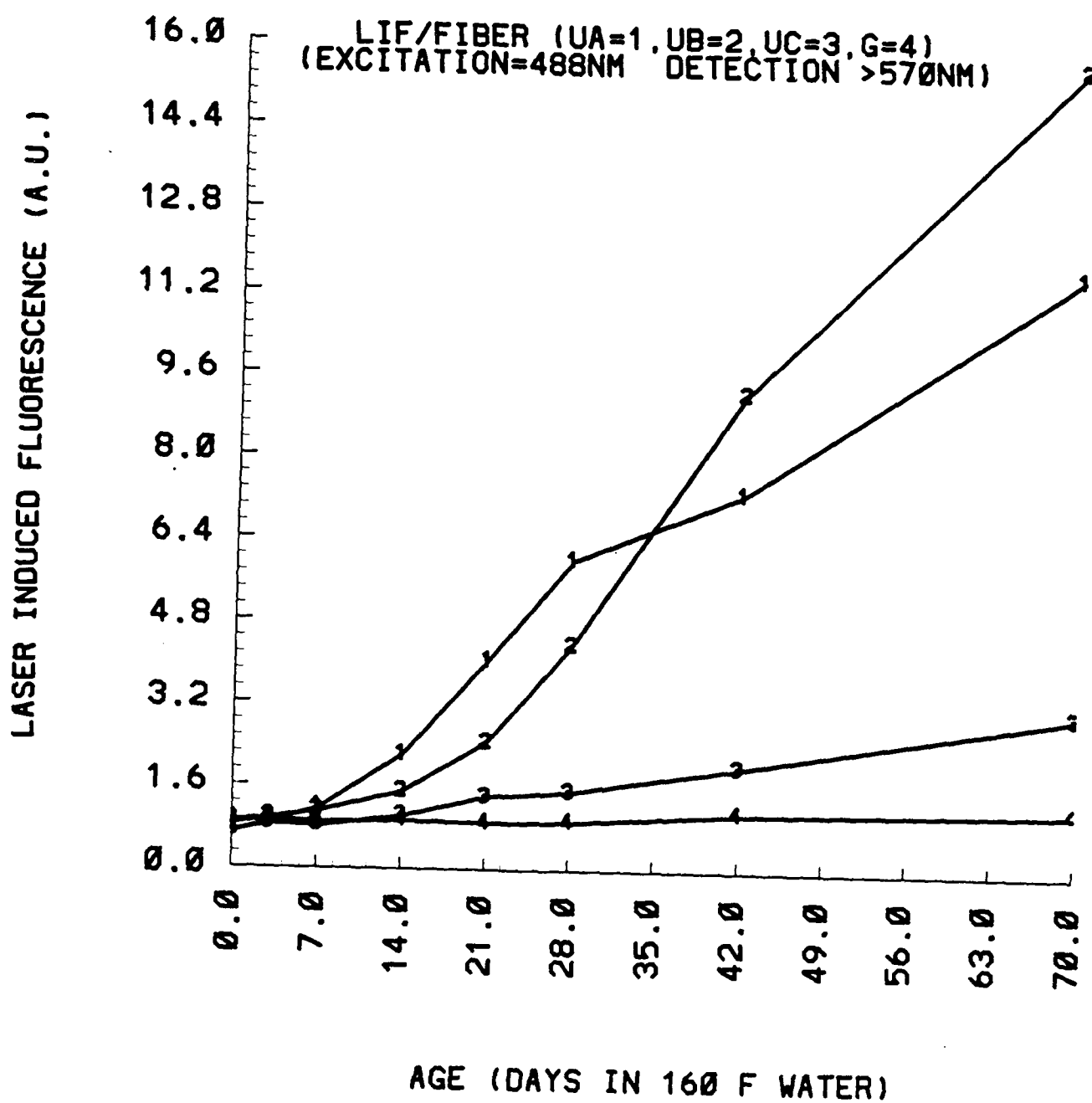


FIGURE 13A. INTEGRATED LASER-INDUCED-FLUORESCENCE INTENSITY MEASURED THROUGH A FIBER-OPTIC BUNDLE AS A FUNCTION OF AGE (Ex: 488 nm; Det: >577 nm; Samples: UA, UB, UC, G; Aging Method: Hot Water)

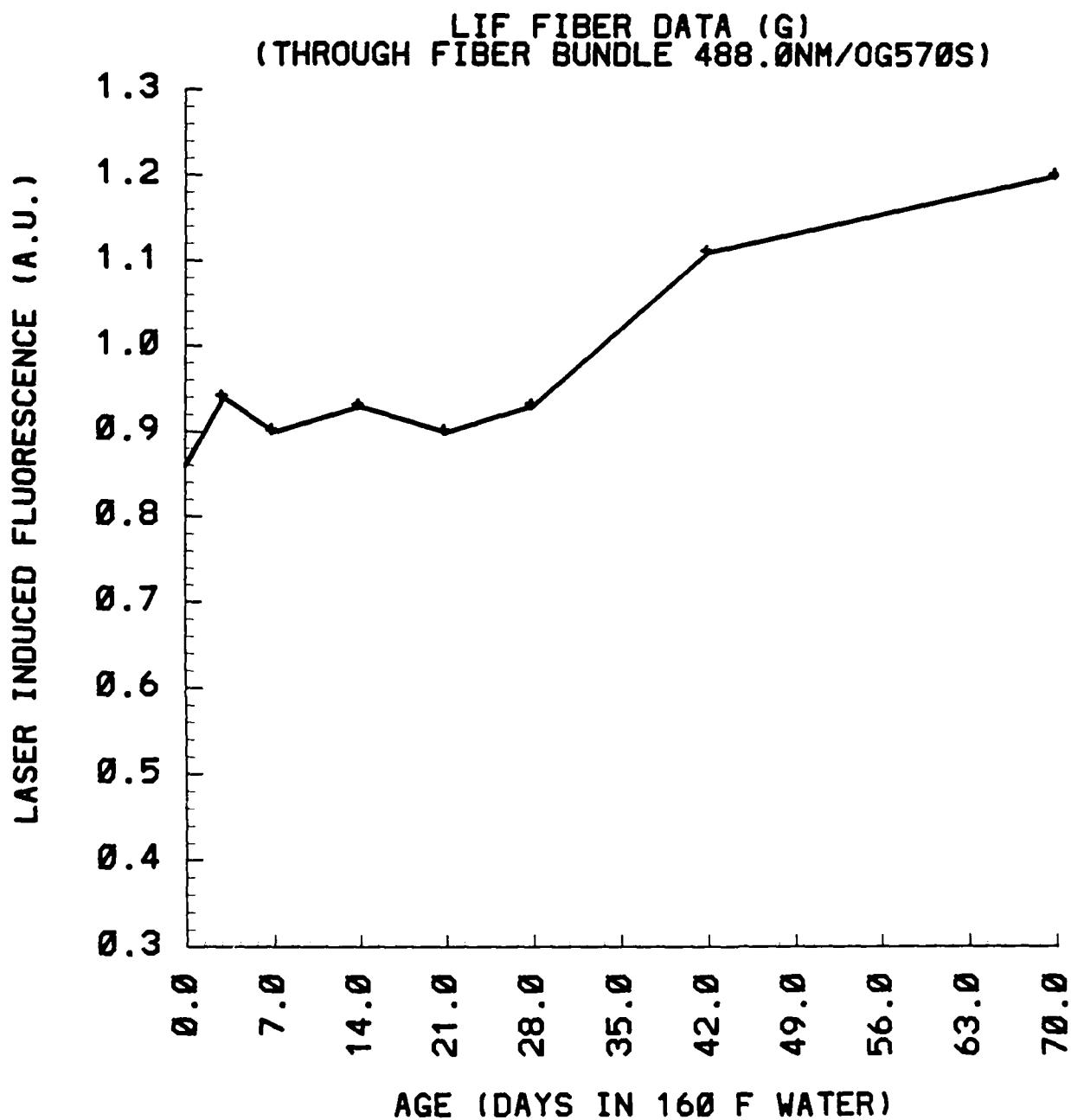


FIGURE 13B. INTEGRATED LASER-INDUCED-FLUORESCENCE INTENSITY MEASURED THROUGH A FIBER-OPTIC BUNDLE AS A FUNCTION OF AGE (Ex: 488 nm; Det: >577 nm; Samples: G; Aging Method: Hot Water; Comments: Expanded scale of Figure 13A)

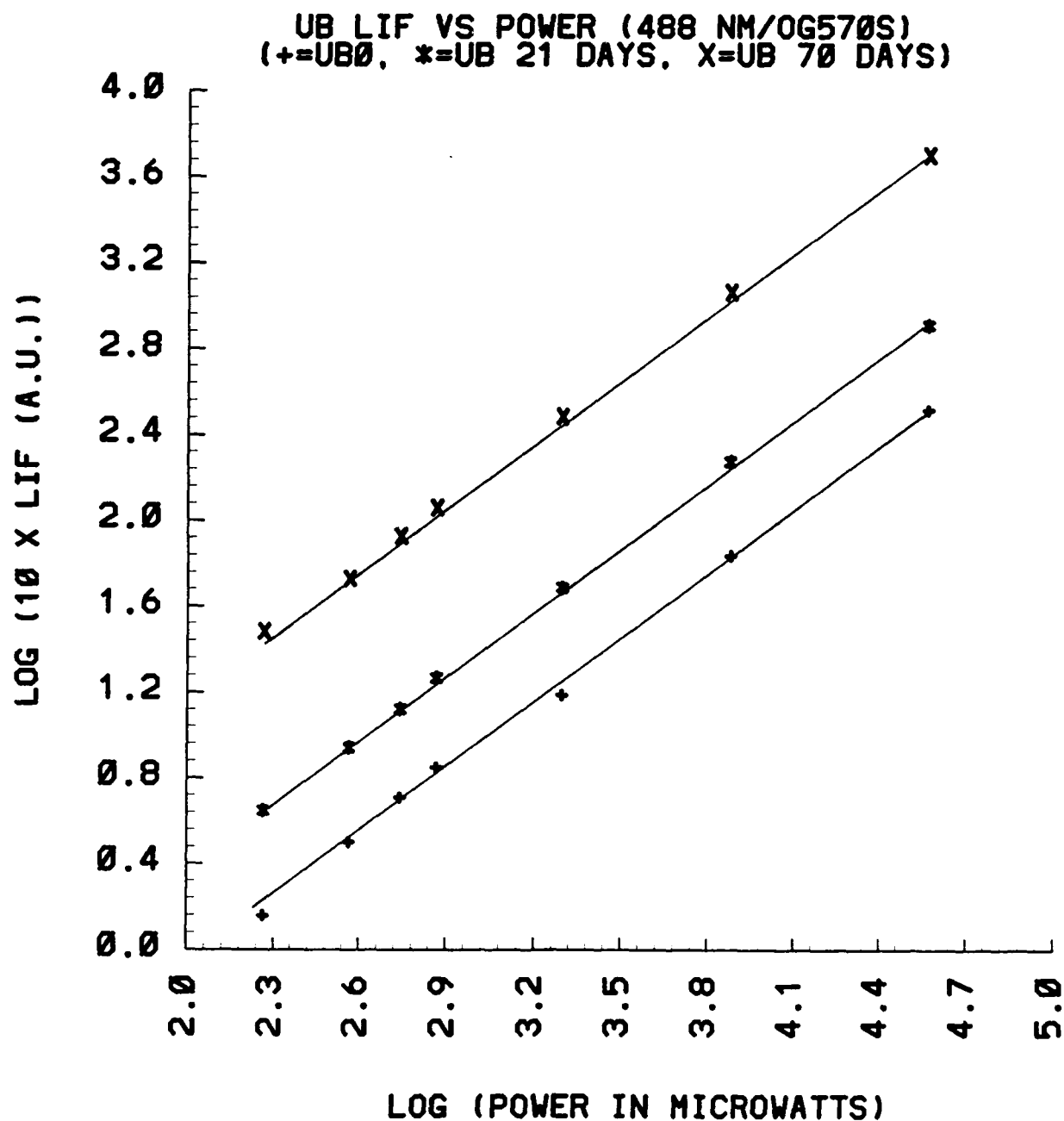


FIGURE 14. LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF LASER POWER (Ex: 488 nm; Det: >577 nm; Samples: UB (unaged), UB (21 days), UB (70 days); Aging Method: Hot Water; Comments: Logarithmic presentation)

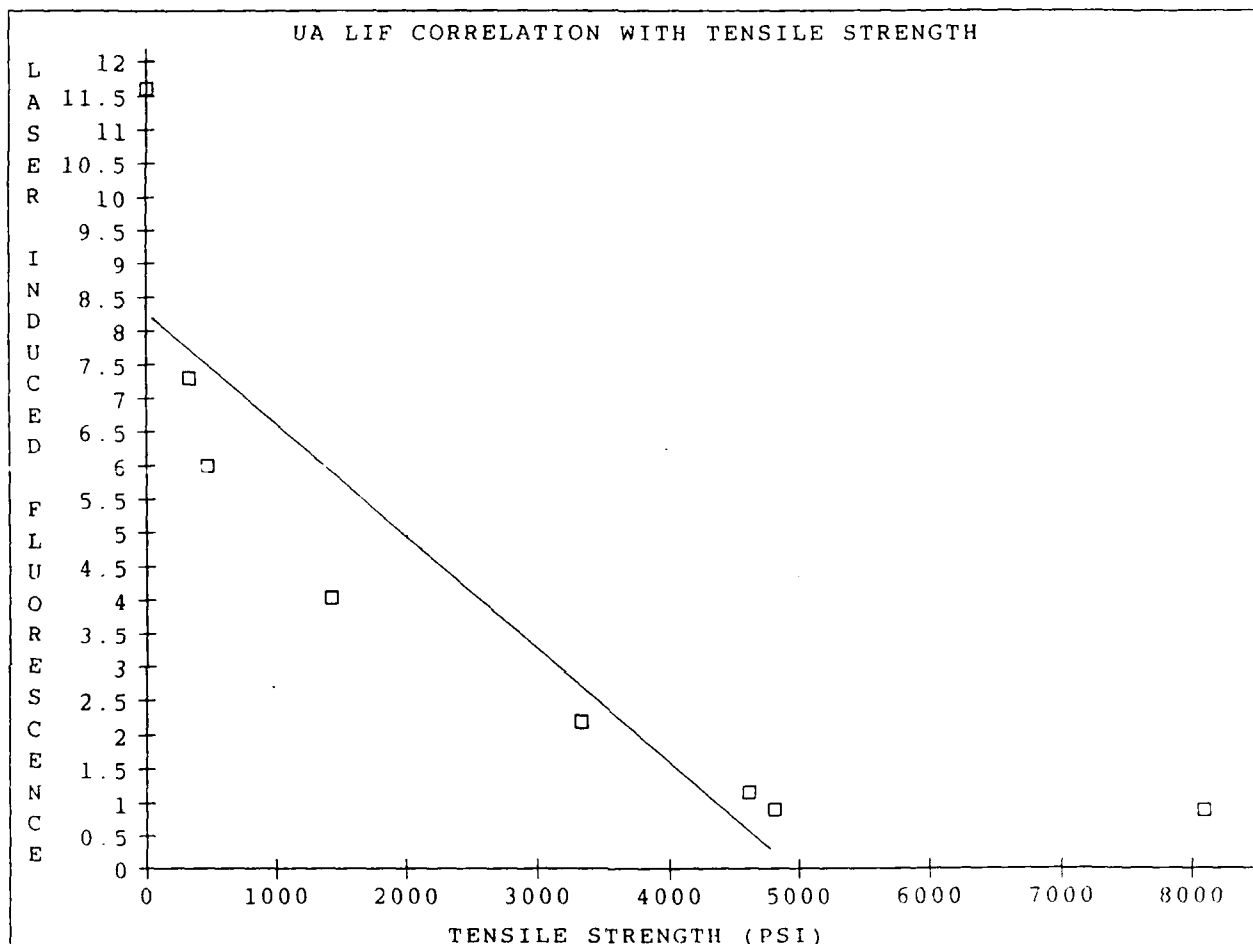


FIGURE 15A. SCATTER DIAGRAM OF LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF TENSILE STRENGTH (Ex: 488 nm; Det: >570 nm; Samples: UA; Aging Method: Hot Water; Comments: Straight line is the linear least-squares fit neglecting data point from the unaged sample)

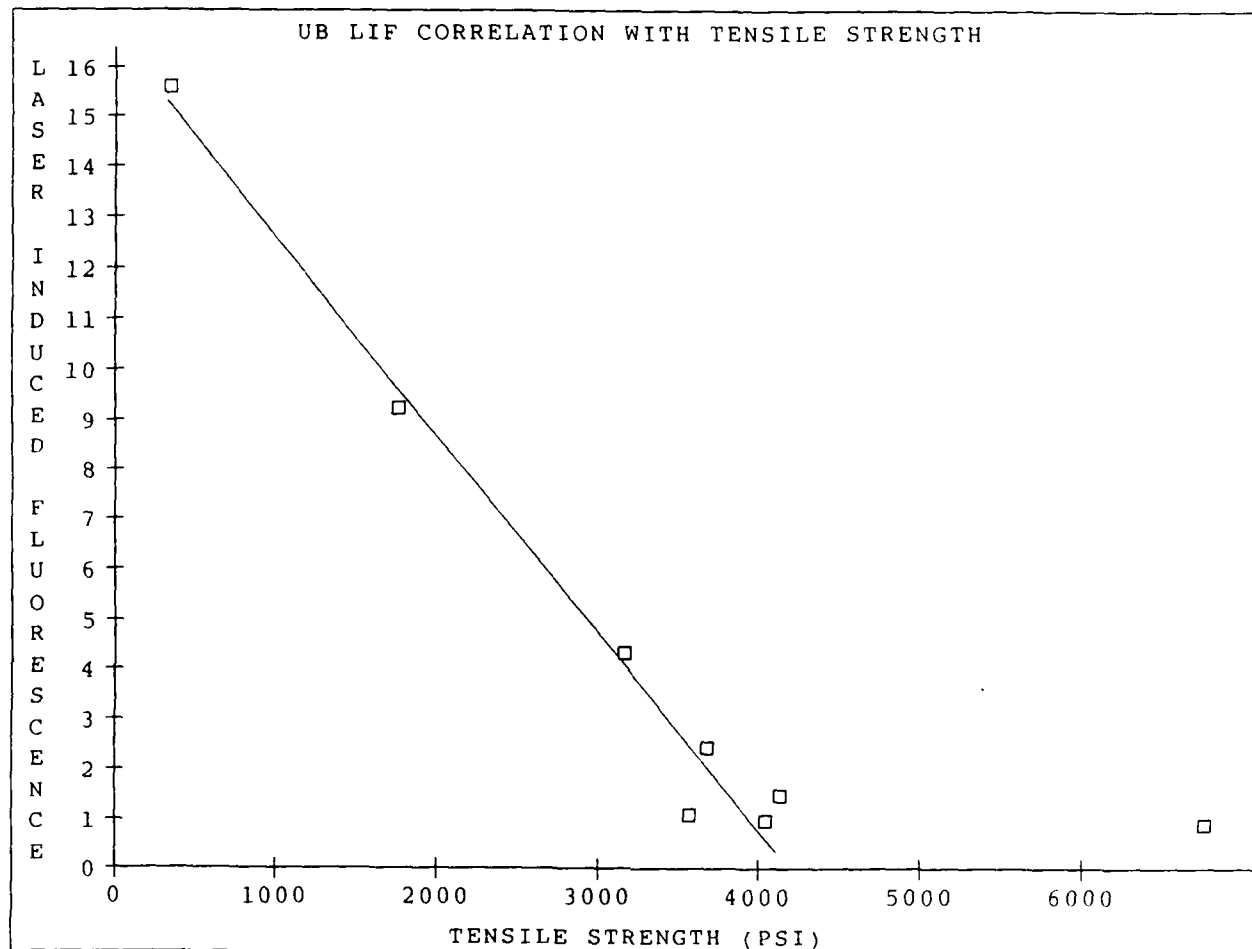


FIGURE 15B. SCATTER DIAGRAM OF LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF TENSILE STRENGTH (Ex: 488 nm; Det: >570 nm; Samples: UB; Aging Method: Hot Water; Comments: Straight line is the linear least-squares fit neglecting data point from the unaged sample)

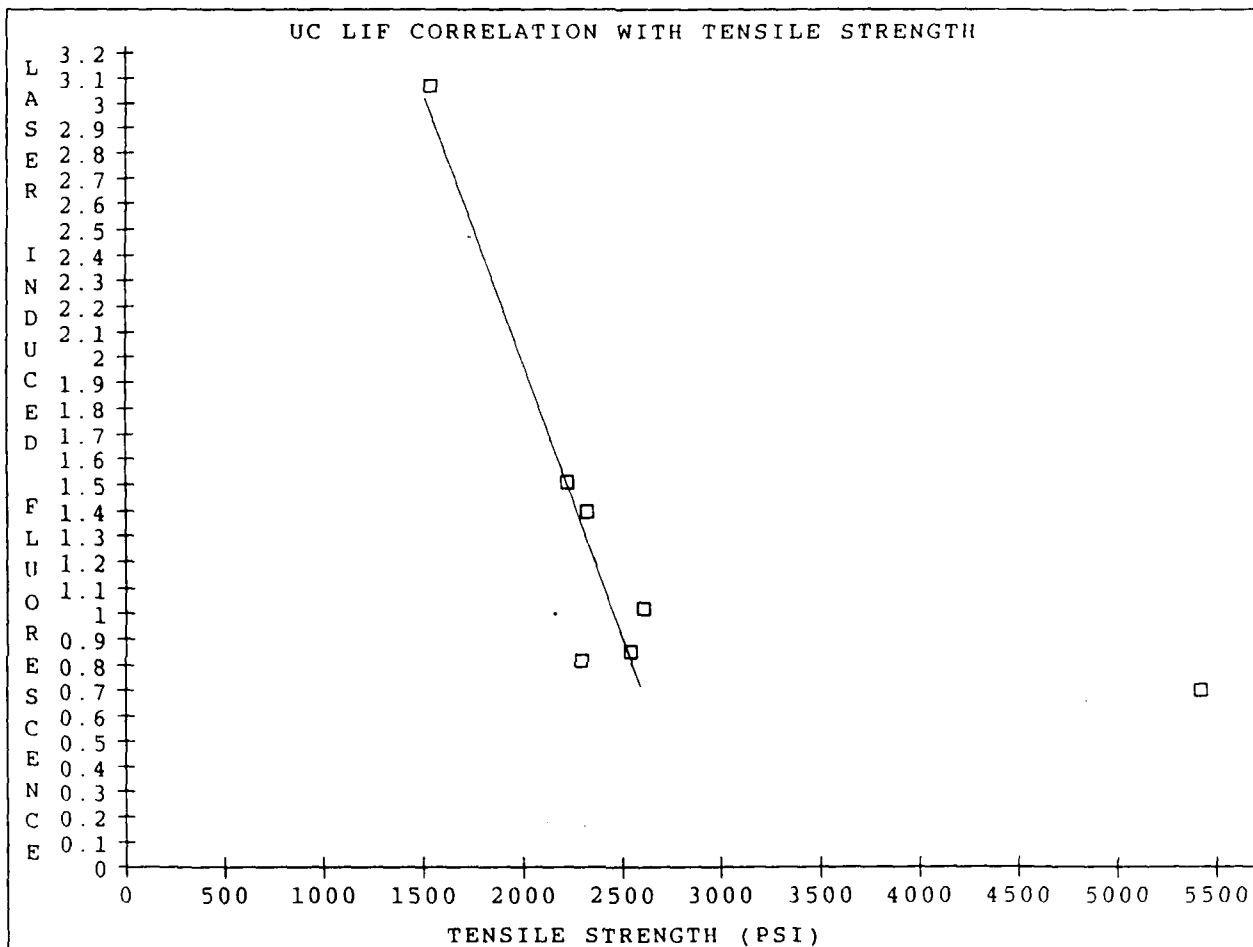


FIGURE 15C. SCATTER DIAGRAM OF LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF TENSILE STRENGTH (Ex: 488 nm; Det: >570 nm; Samples: UC; Aging Method: Hot Water; Comments: Straight line is the linear least-squares fit neglecting data point from the unaged sample)

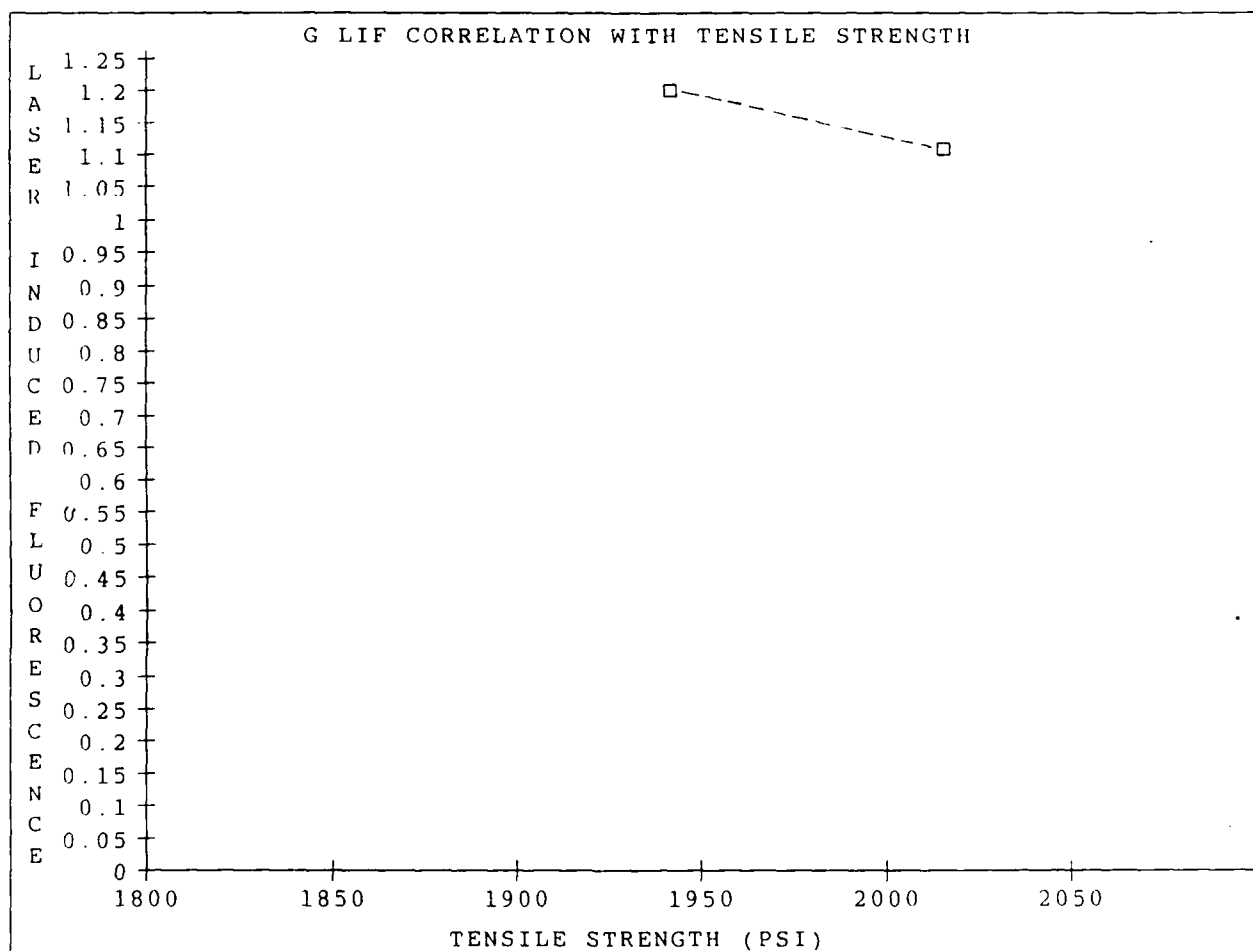


FIGURE 15D. SCATTER DIAGRAM OF LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF TENSILE STRENGTH (Ex: 488 nm; Det: >570 nm; Samples: G; Aging Method: Hot Water; Comments: Straight line is for ease of viewing, see text for discussion)

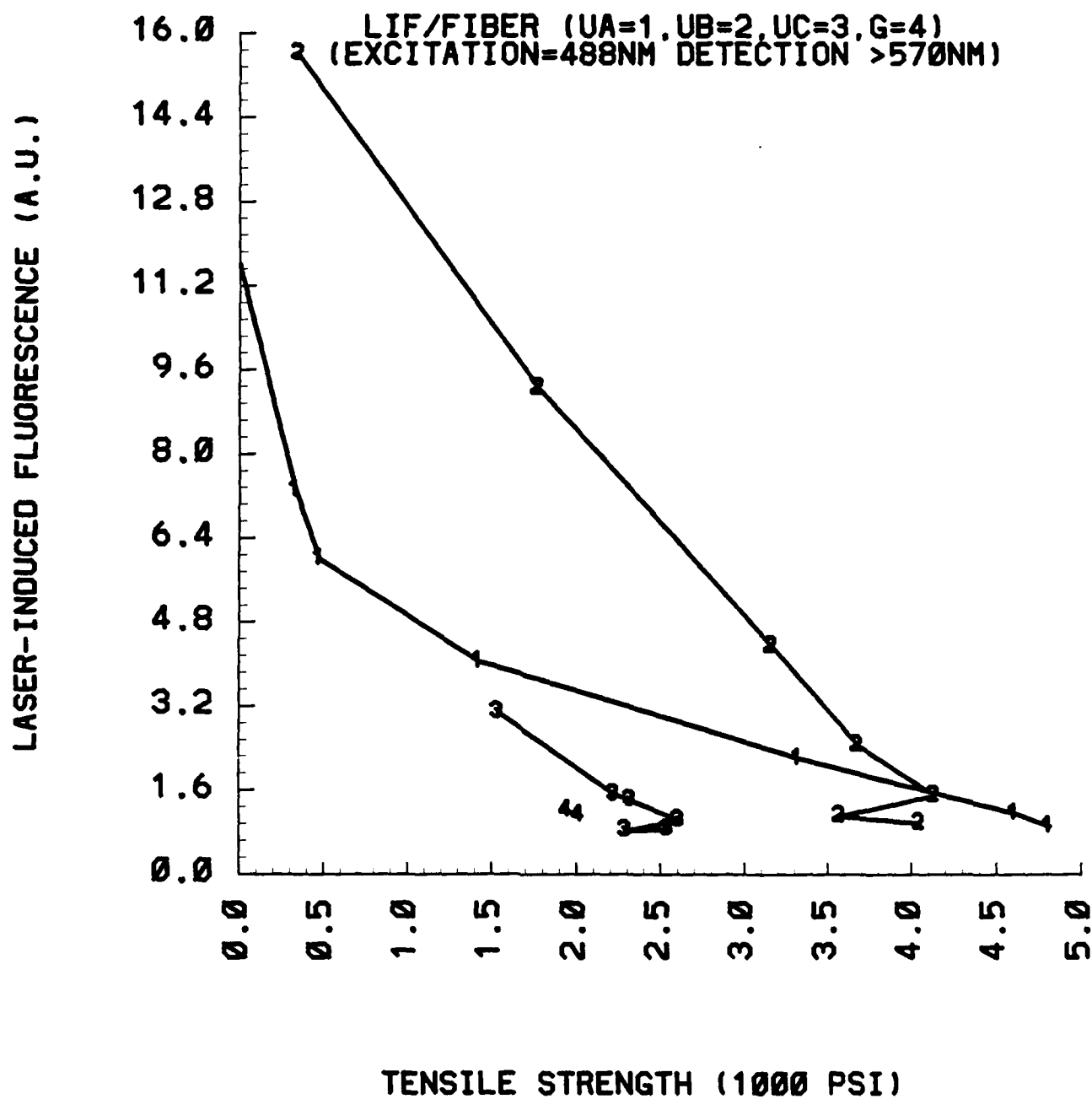


FIGURE 15E. SCATTER DIAGRAM OF LASER-INDUCED-FLUORESCENCE INTENSITY AS A FUNCTION OF TENSILE STRENGTH (Ex: 488 nm; Det: >570 nm; Samples: UA, UB, UC, G; Aging Method: Hot Water; Comments: Data displayed are those of the previous scatter diagrams, with the data points simply connected for ease of viewing)

LASER-INDUCED-FLUORESCENCE DETECTOR CONCEPTUAL DIAGRAM

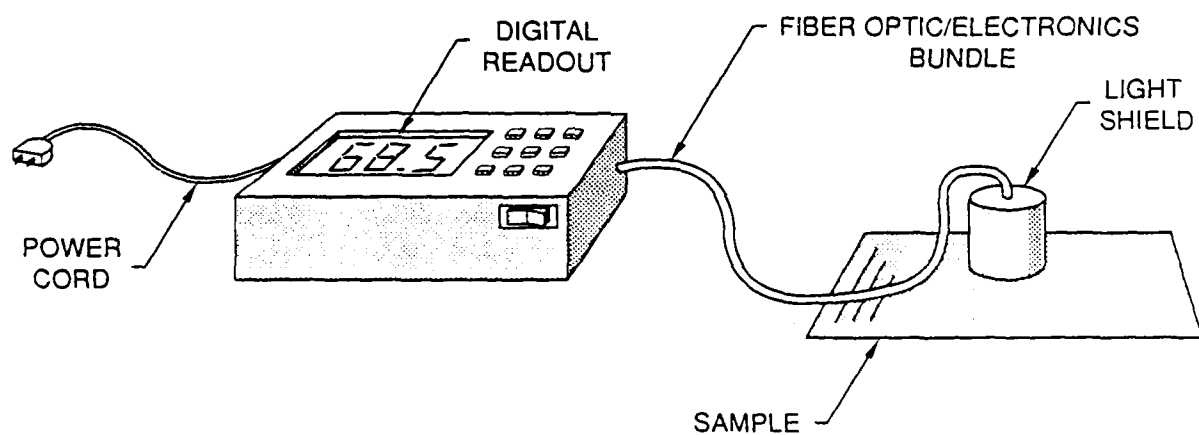


FIGURE 16. CONCEPTUAL DIAGRAM OF PROPOSED DEVELOPMENTAL PROTOTYPE

APPENDIX

Table A1. COLORS OF UNAGED SAMPLES (1931 CIE standard color definitions using illumination standard "C")

Sample	Y	x	y
UA	27.7	0.443	0.432
UB	26.0	0.447	0.433
UC	25.6	0.443	0.430
G	26.4	0.422	0.417
GF	25.8	0.413	0.408
PU1	2.0	0.297	0.290
PU1S	10.5	0.392	0.363
PU2	8.0	0.297	0.301
PU2S	3.0	0.349	0.343
EST-5708	36.1	0.422	0.414
LU1	13.6	0.283	0.290
LU2	11.1	0.302	0.307